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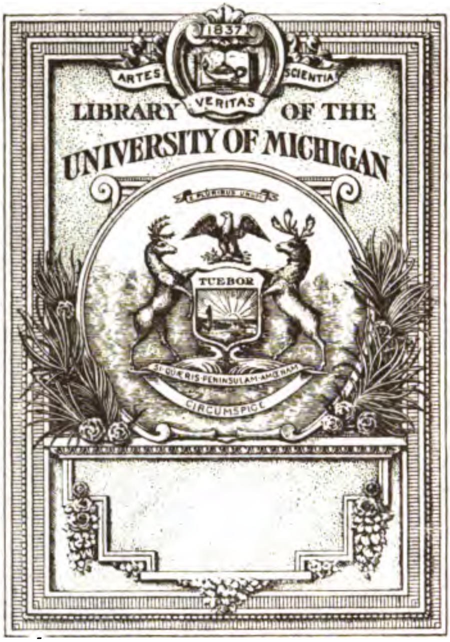

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LABORATORY MANUAL

OF

ELEMENTARY CHEMISTRY

BY

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GEORGE WAHR, PUBLISHER.
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PREFACE.

This manual is intended for a laboratory guide in connection with a larger text or a course of illustrated lectures. It calls for no work which may not be done by the average high school student and with the average laboratory equipment. It is complete enough so that it may be used for two years' work, one being devoted to general and the other to analytical chemistry.

In preparing this second edition the authors have changed the original plans in several important respects. The non-metallic portion has been much amplified, both experiments and explanations being increased. The questions which cover the experiments are not in any sense complete. They are intended solely to suggest to teacher and pupil other questions which may be answered by observation of the experiment at hand.

The metallic section is almost entirely new, being modelled in part after the new qualitative analysis of Prof. J. F. McGregory, of Colgate University. The authors have a very high opinion of the educational value of analytical chemistry and for that reason the work is quite complete in this section. It is not complete enough to give a student a technical training, but if carefully followed out will lay a broad foundation for further technical study. Chemistry in secondary schools should make for general education and culture rather than for technical training, and in the minds of the authors no part of the work tends to develop keen powers of observation so much as the experiments of blow-pipe and wet analysis.

The blow-pipe analysis precedes the wet work because it teaches the student to be careful in small details and this care aids in the later and more complex study of the separations.

In teaching the metals and their reactions the authors have found that the practice of writing the equations for all reactions aids the student in remembering what he has done. In our own laboratory this has been insisted upon with good results. After the chief reactions have been verified experimentally a series of unknowns of fifty or sixty has been given to the class and each student has been required to find the one metal in solution, using methods of his own. It should be understood by the student that in working out these unknowns his chief aim is to learn the reactions which are involved rather than to simply find the metal.

The portion of the analytical work dealing with the separations needs no special explanation as the methods are the same as those generally employed.

The authors wish to acknowledge their indebtedness to Prof. J. F. McGregory, of Colgate University, for many suggestions and corrections, to Mr. E. L. Paige for the photographic work, and to others who by the inspiration of their encouragement have made the work a pleasant task.

Any corrections or suggestions by the teachers using the work will be gratefully received.

Colgate University,
Hamilton, New York.

August 11, 1904.

TABLE OF ATOMIC WEIGHTS.

Aluminum	27.1	Molybdenum	96.
Antimony	120.	Neodymium	144.
Argon	40.	Nickel	58.7
Arsenic	75.	Nitrogen	14.04
Barium	137.4	Osmium	191.
Bismuth	208.5	Oxygen	16.00
Boron	11.	Palladium	106.
Bromine	79.96	Phosphorus	31.
Cadmium	112.	Platinum	194.8
Caesium	133.	Potassium	39.15
Calcium	40.	Praseodymium	140.
Carbon	12.00	Rhodium	103.
Cerium	140.	Rubidium	85.4
Chlorine	35.45	Ruthenium	101.7
Chromium	52.1	Samarium	150.
Cobalt	59.	Scandium	44.1
Columbium	94.	Selenium	79.1
Copper	63.6	Silicon	28.4
Erbium	166.	Silver	107.93
Fluorine	19.	Sodium	23.05
Gadolinium	......	Strontium	87.6
Gallium	70.	Sulphur	32 06
Germanium	72.	Tantalum	183.
Glucinum	9.1	Tellurium	127.
Gold	197.2	Terbium	......
Helium	4.	Thallium	204.1
Hydrogen	1.01	Thorium	232.
Indium	114.	Thulium	......
Iodine	126.85	Tin	118.5
Iridium	193.	Titanium	48.1
Iron	56.	Tungsten	184.
Lanthanum	138.	Uranium	239.5
Lead	206.9	Vanadium	51.2
Lithium	7.03	Ytterbium	173.
Magnesium	24.36	Yttrium	89.
Manganese	55.	Zinc	65.4
Mercury	200.3	Zirconium	90.6

NONMETALLIC ELEMENTS.

MATTER DEFINED.

All the objects which our senses can recognize occupy space. Likewise all are drawn toward the earth by a force which we call gravitation. The measure of this force we call weight. *Matter* is the general name applied to all objects and may be defined as that which occupies space or which has weight.

CONDITIONS IN WHICH MATTER EXISTS.

EXPERIMENT 1. Note the properties of a piece of ice. Place the ice in a small flask and melt. Next boil the water thus made. What is formed? Here we see that matter exists in at least three conditions. Can you think of any others?

DIVISIONS OF MATTER.

Scientists believe that all forms of matter are composed of very small particles. These particles they call *molecules*. An aggregation of these molecules is called a *mass*. We can know matter in the mass form only, as the molecules are too small to appeal to our senses. Most molecules have properties that seem to indicate that they are composed of still smaller particles. These smaller particles we call *atoms*.

We may divide a mass of sugar, for example, into two pieces, these two into other two, and so on almost indefinitely. We can conceive however that after an almost infinite number of divisions the sugar can no longer be divided by such a method. This smallest piece of sugar would be the molecule. Under certain circumstances as we will see in later experiments, the sugar mass can be disintegrated into the several constituents of which it is composed. We can conceive that the same change could take place in the smallest particle. The constituents into which the sugar would be divided are the atoms. In other words, the smallest particle of sugar capable of existing as such, is the molecule, while the constituents which together make up the molecule of sugar would be the atoms.

The above conception of matter forms the basis of the theory known as the atomic theory.

NONMETALLIC ELEMENTS.

PHYSICAL AND CHEMICAL CHANGE.

Exp. 2. Dissolve a small quantity of sugar in water. Evaporate the solution to dryness in a small porcelain dish on a water bath and examine the residue. Has the sugar changed?

Heat a little sugar strongly and examine again. Has it changed this time?

Exp. 3. Heat a small piece of nickel wire un-

til red hot. Allow to cool and examine. Is it still nickel?

Place some nickel in a test tube and pour water on it until it is covered. Now add, drop by drop, concentrated sulfuric acid until bubbles of gas arise from the wire. After allowing the tube and contents to stand a few minutes the nickel will disappear. Next filter the contents of tube and evaporate to dryness. Examine the residue. What has happened to the wire?

Exp. 4. Heat a piece of platinum wire, a piece of magnesium wire or ribbon. What is the difference in action?

PHYSICAL AND CHEMICAL CHANGES DEFINED.

If we heat a piece of nickel to redness then allow it to cool we will find that it is still nickel, it has not changed. This is a good example of physical change and we may define a physical change as one such that when the causes of the change have been removed the substance *returns* to its original condition. In other words a physical change is one which *does not destroy* the identity of matter.

On the other hand, if we subject the piece of nickel to the action of an acid such as sulfuric, it will disappear and we have a substance in its place which in all its outward properties is not at all like nickel. Its identity has been completly destroyed.

This is a type of chemical change and we may define a chemical change as one such that when the causes have been removed the substance *does not return* to its original condition. Or, a chemical change is one in which the identity of the substance *is destroyed.*

We have already seen that all matter is regarded as composed of very small particles, molecules and atoms. We have learned that when large masses of matter are subjected to certain conditions they may be separated into their constituents. We believe that the same is true of molecules as of masses. These constituents of molecules are the atoms. Molecules, then, are built up by the combination of atoms. Masses are made by the aggregation of molecules.

With the above in mind we are ready for a new definition of chemical and physical change. *That which produces a change in matter without destroying the identity of the molecule is a physical change, and that which alters the molecule or decomposes it into its atoms is a chemical change.*

MIXTURES AND CHEMICAL COMPOUNDS.

Exp. 5. Mix a small quantity of sand with common salt. Can you distinguish the two? Place the mixture in a porcelain dish and pour about 20 cubic centimeters of hot water on it. Filter the solution. What remains on the filter paper? Evaporate the solution to dryness. What

is the residue? Here we have an example of a mixture and at the same time an example of a physical change.

Exp. 6. Mix equal quantities of fine iron filings and powdered sulfur. Examine with a magnifying glass. Can the elements be distinguished? Treat a sample of the mixture with carbon disulfid, filter and examine the residue in the filter paper. Where is the sulfur? Place another sample in a test tube and heat. When the action has ceased, break the tube and examine the contents. Is the substance like either of the constituent substances? Can you separate the constituents as you did before heating!

Cubic Centimeter is usually abbreviated c. c.

State the difference between a mixture and a chemical compound.

THE COMMON ELEMENTS AND THEIR COMPOUNDS.

DEFINITION.

An *element* is a substance which cannot be separated by any known method into two or more different substances.

CLASSIFICATION.

There are about 75 elements known. A complete list is given at the beginning of this book. They are divided into two great classes called the

metals and the *non-metals* being so classed because of characteristic physical and chemical properties. For example the metals generally have a high specific gravity they are usually hard, have metallic lustre, etc. These properties are usually lacking in the case of the non-metals although a few possess them. The line of distiction between the two classes as determined by their physical properties is not very clear.

The chief chemical property of the metals is that they combine with the non-metallic element *oxygen* or with oxygen and hydrogen to form a class of substances called *bases* while non-metals combine with the same elements to form a class of compounds having properties very different from those of the bases. These are known as *acids.*

See the definition of bases and acids.

GROUP OF ELEMENTS.

There are certain elements which show many common or similar properties. Such are usually classed together, the groups being named from some common important element or from some property common to the whole group. Thus we have the Oxygen Group, the Halogen Group, etc.

NAMES AND SYMBOLS OF THE ELEMENTS.

The names of the elements have been derived from a variety of sources, from some characteristic property, from some place or country, from mythology etc. Each element is designated by a symbol

peculiar to itself. In the early days of chemical work, chemistry and astrology were closely allied and the earliest symbols for the elements were the astrological signs for planets. Now we designate the elements by one or two letters of their names, one when the name of one element only begins with the letter and two when several elements have names beginning with the same letter. Thus the element arsenic has the symbol As and the element silver the symbol Ag.

Ten of the elements derive their symbols from their Latin names, antimony, Sb, Stibium, copper, Cu, Cuprum, gold, Au, Aurum, iron, Fe, Ferrum, lead, Pb, Plumbum, mercury, Hg, Hydrargyrum, potassium, K, Kalium, sodium, Na, Natrium, tin, Sn, Stannum, and tungsten, W; Wolframium.

The above symbols are generally used to designate a single atom of the element and should be so understood.

CHEMICAL FORMULAS.

Definition.—A formula is a character designating a chemical compound. It is to the compound just what the symbol is to the element. It is made by combining in the proper proportions the symbols of the elements which make up a compound.

We may write formulas in two ways. We may repeat the symbols of the elements as many

times as they occur or we may place after each symbol an index number to show how many times that particular element occurs in the compound. For example a molecule of sulfuric acid is composed of three elements viz. hydrogen, sulfur and oxygen. It has been proved by many careful experiments that these occur in the ratio of two atoms of hydrogen, H_2, one atom of sulfur, S and four of oxygen, O_4. Hence we might write the formula thus HHSOOOO. Such a method is very cumbersome, so we write the symbols and place after each a number to show how many times it should be written i. e. H_2SO_4. This is called an empirical formula and is most used to write simple compounds.

There is another kind of formula that is used to designate very complex compounds such as are found in the branch of our science called Organic Chemistry. This will be discussed in a later paragraph.

MODERN NOMENCLATURE.

In 1787 the French chemist Lavoisier made the first attempt to introduce a systematic method of naming the elements and their compounds and his system is the basis of the one now in use. The names of the older elements and of many of their compounds were not changed, but as fast as new were discovered they were named according to the

system. All new *metals* receive names ending in *ium* and new *non-metals* those ending in *on*.

Those compounds made up of two elements are called *binary* compounds and in naming them we name the metal first, then the non-metal, changing the last one or two syllables of its name to *id*. Thus NaCl is a binary compound. It is made up of *sodium* (Na) and *chlorin* (Cl) and is called *sodium chlorid*.

If the same two elements combine to form two different compounds the name of the metal is so changed as to show which of the two contains the greater amount of non-metal. Thus we have two compounds of *iron* (Fe) and *chlorin*, (Cl). $FeCl_2$ and $FeCl_3$ both iron chlorids. The first is called *ferrous chlorid* and the other *ferric chlorid*. The termination *ous* indicates the lesser quantity of non-metal and *ic* the greater.

THE ACIDS.

Definition. An acid may be defined as a compound of hydrogen and a non-metal usually in combination with oxygen. Part or all of the hydrogen may be replaced by a metal. An acid has a sour taste and will turn red certain vegetable coloring matters such as litmus.

There are two great classes of the acids, the halogen acids (named from the Halogen Group of elements) and the oxyacids. The halogen acids are compounds of the elements hydrogen and

one of the halogens. They are binary compounds and are named as such except that the name of the non-metals ends in *ic*. Thus HCl is a compound of hydrogen and chlorin and is called *hydrochloric acid*.

The oxyacids are compounds of three elements two of which, oxygen and hydrogen, are common to all. These are combined with a third nonmetallic element which gives its name to the acid. The name terminates in *ous* or *ic* as in the case of binary compounds, the acid having the lesser amount of oxygen ending in *ous* and the greater in *ic*. Such are H_2SO_3 and H_2SO_4 both acids of *sulfur* (S) and named *sulfurous* and *sulfuric* acids.

Sometimes the oxygen exists in more than two proportions as in certain acids of chlorin, $HClO$, $HClO_2$, $HClO_3$ and $HClO_4$. The name of the most important ends in *ic*. This is $HClO_3$, chloric acid. $HClO_2$ is chlorous. $HClO$ contains less oxygen than chlorous acid and has before its name the prefix *hypo* meaning *under*, thus is named *hypochlorous* acid. $HClO_4$ contains more oxygen than chloric acid and is named *hyper* or *perchloric* acid. Hyper or per means *over*.

NOTE. There are still other acids which do not fall in these two classes, they are composed of other elements of the oxygen family with hydrogen such as H_2S (hydrosulfuric acid) etc.

Bases.

(See definition P. 27.)

Bases are named like binary compounds. For example K_2O, a compound of potassium and oxygen, is called potassium oxid. Some bases contain more than two elements and strictly speaking are not binary compounds. Such a base is KOH, potassium hydroxid. Here the OH group is considered as a single element and is named *hydroxyl*. A group of elements which acts like a single element, is known as a compound *radical*.

Salts.

A salt is derived from an acid by replacing the hydrogen of the acid by a metal. The name of the salt comes from the acid from which it was made. Acids whose names end in *ic* give rise to salts the names of which end in *ate*. Those ending in *ous* make salts ending in *ite*. There are two salts of sodium derived from sulfurous and sulfuric acids written Na_2SO_3 and Na_2SO_4 named *sodium sulfite* and *sodium sulfate* respectively. If the acid name has a prefix the same prefix will appear in the name of the salt. $HClO_4$ (perchloric acid) gives rise to the sodium salt $NaClO_4$ which is called *sodium perchlorate*.

In a salt the name of the metal remains unchanged except when it forms two compounds with the same acid then the name is changed as in binary compounds. For example there are two compounds of the metal iron, Fe, and sulfuric acid,

$FeSO_4$ and $Fe_2(SO_4)_3$. These are named *ferrous* and *ferric sulfate.*

The salts of the halogen acids are an exception to the above rule. They are binary compounds and are named as such. Thus NaCl, a salt from hydrochloric acid, is not called sodium hydrochlorate according to the rule but is named sodium chlorid.

NOTE.—Certain combinations of the elements act like a single element and form salts in much the same way as the metal. Such a combination is called a radical.

ATOMIC WEIGHT.

It is universally believed that the atoms differ in weight and that each has a constant weight. This cannot be determined absolutely but can be with relation to some other element taken as a standard. This standard is the lightest element, hydrogen. Thus *the atomic weight of an element may be defined as the weight of its atom as compared with the weight of an atom of hydrogen.* The methods by which these conclusions are reached are beyond our comprehension at this stage of our work.

NOTE.—As hydrogen combines with comparatively few elements, it is more convenient to use oxygen as the standard of atomic weight. For this purpose the ratio between the weights of hydrogen and oxygen has been carefully determined. If H is assumed as unity, O has a weight of exactly 15.88. But more often oxygen is taken as the standard and its atomic weight is assumed as 16 and hydrogen then has an atomic weight of 1.0075.

HYDROGEN.

Symbol H. Atomic weight 1.

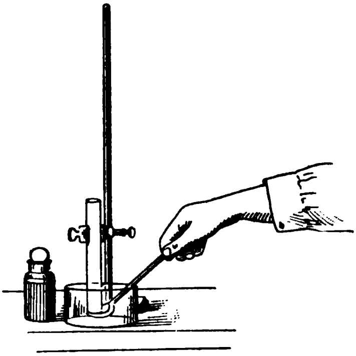
Discovered in 1766 by the English chemist, Cavendish. The name comes from the Greek, meaning "a water former."

PREPARATION.

Hydrogen made by the decomposition of water.

Certain elements, such as the metals, potassium (K) and sodium (Na), have the power to decompose water, setting free its hydrogen. We find by experiment that water is composed of two parts by volume of hydrogen to one part of another element called oxygen, and is designated by the formula H_2O. (See p. 29.)

Exp. 7-a. Fill an evaporating dish or pan with water. Fill a bottle or large test tube with water. Cover the tube with a glass plate, invert in the dish and remove plate. Wrap a small bright piece of sodium in a piece of dry tissue paper or wire gauze then with a dry pair of forceps hold the sodium under the mouth of the tube. Note the formation of gas.



When the evolution of gas has ceased, test the contents of the tube by thrusting into it a burning match. The gas burns at the mouth of the tube but the match is extinguished if thrust into the gas.

Such a gas which will not support burning is called a non-supporter of combustion. This is the test usually applied to determine hydrogen.

b. Test the water used in the above experiment with red litmus paper. The color is changed to blue. Rub some of the liquid between the thumb and forefinger. Note the greasy feeling. Taste the liquid. It has a peculiar soapy taste. These are the properties characterizing a class of substances called bases.

Definition: *Bases* are compounds of the metals with oxygen or with oxygen and hydrogen. Certain of them are soluble in water and such are called *alkalies.* Potassium and sodium hydroxids, KOH and NaOH, are typical alkalies.

Explanation of the action between sodium and water.

Sodium is a metal which has so strong an attraction or *affinity* for oxygen that it will take the element from any of its compounds. Water is composed of hydrogen and oxygen. The sodium combines with the oxygen forming a base Na_2O, setting the hydrogen free. The base is soluble in water with which it at once combines to form an alkali, *sodium hydroxid* (NaOH).

NOTE—Litmus paper is paper colored with an organic substance which is changed red by acids and blue by bases. If the litmus paper on your table is red and you wish it blue, hold it over the mouth of the ammonia bottle. If the opposite change is desired hold it over the hydrochloric acid bottle.

Represented graphically the reaction is as follows:

1. Water is composed of oxygen and hydrogen.
2. Sodium with water gives sodium oxide and hydrogen.
3. Sodium oxide with water gives sodium hydroxid.

The above is a very cumbersome way of writing a reaction so it is never used except for explanation. Written in chemical terms it is as follows:

1. Water is H_2O.
2. 2Na with H_2O gives Na_2O and H_2.
3. Na_2O with H_2O gives 2NaOH.
4. This is further simplified by substituting for the words "with," "gives," etc., the plus and equality signs. Thus we have

2. $2Na + H_2O = H_2 + Na_2O$.
3. $Na_2O + H_2O = 2NaOH$.

This form of writing the reaction is called an equation.

NOTE—Reactions. When two or more substances act upon each other to form new substances the process is called a reaction.

Caution. Sodium is a metal which combines very readily with water with evolution of hydrogen. The reaction is almost explosive, but if small, bright pieces of the metal is used there is little danger. Before use therefore always see that the

metal is bright and clean. Sodium is kept under benzine to prevent it from combining with the moisture of the air.

CHEMICAL EQUATIONS.

When substances act upon one another to form new substances the process is called a reaction and is stated in a form known as a chemical equation. The materials which take part in a reaction are placed before a sign of equality and are called the "factors," while the resulting substances are placed after the sign and are called "products."

The quantity of matter in the universe is constant. None is created and none is destroyed. This fact is shown in the chemical equation, since the sum of the products always exactly equals the sum of the factors. For example in the equation $H_2+O=H_2O$, the atomic weight of hydrogen is 1 and that of oxygen is 16, and the equation represents this fact, that two atoms of hydrogen with an atomic weight of 1 each, will combine with one atom of oxygen forming a product having a weight of 18, the sum of the weights of the two factors.

MOLECULAR WEIGHT DEFINED.

The above quantity 18 is known as the molecular weight of water and the molecular weight of a compound may be defined as the sum of the atomic weights of the elements composing that compound.

Another example will help to make this point

clear. Pure limestone or chalk is composed of the three elements, calcium, carbon and oxygen, and has the formula $CaCO_3$. If this is heated it may be easily proved by analysis that two products are formed, calcium oxid, CaO and a compound of carbon and oxygen called carbon dioxid CO_2. The equation would be as follows:

$$CaCO_3 \text{ heated} = CaO + CO_2.$$

This means when fully expressed that 100.1 parts $CaCO_3$ [$Ca(40.1)+C(12)+3O(3\times16)=100.1.$] when heated will give 56.1 parts CaO $(40.1+16.)$ and 44 parts CO_2 [$12+32(2\times16.)$] The accuracy of these quantities has been established by many careful analyses.

In many equations a student will notice that a numeral is placed before one or more of the products or factors, as for example $Na_2O+H_2O=2NaOH$. Here a 2 is placed before the formula NaOH in order that there may be the same number of atoms and hence the same weights on the two sides of the equation. Such an equation is said to be "balanced." Another way of expressing this is to say that each atom in the products must appear in the factors.

VALENCE.

All of the non-metallic elements form compounds with hydrogen and if these are compared it will be found that they fall into four classes. They

combine with one, two, three or four atoms of hydrogen respectively. In other words each nonmetallic element has a definite power to combine with this one element. This combining power is called the *valence* of an element.

The unit of valence is the hydrogen atom, thus hydrogen is univalent. All the elements having the power to combine with or replace one atom of hydrogen are univalent. Those which can combine with two, three or four atoms are bivalent, trivalent and quadrivalent respectively. Elements have another class name depending on their valence, i. e., those having a valence of one are called *monads, of 2, 3 and 4, dyads, triads and tetrads.*

The metals differ from the non-metals in that they do not commonly form compounds with hydrogen. Their valence may be determined however by the combinations which they form with the non-metals of which the valence is known in every case. For example the metal sodium does not form any combination with hydrogen but it does with chlorin, a univalent element.

As the combination is in the ratio of one to one, sodium is a univalent element.

Usually in writing symbols the valence of the atoms is not expressed, but if for any reason this is desirable it may be indicated by Roman numerals, a series of short lines or accents as follows :

$$\overset{I}{\mathrm{Cl}} \quad \overset{II}{\mathrm{O}} \quad \mathrm{N}\equiv \quad \mathrm{Ca}= \quad \overset{IV}{\mathrm{Si}} \quad -\overset{|}{\underset{|}{\mathrm{C}}}- \quad \mathrm{Cl}' \quad \mathrm{O}'' \quad \mathrm{N}'''$$

These marks which indicate the combining or "affinity" units are called "affinity bonds." When atoms unite to form compounds these bonds must be "satisfied," i. e. each atom must have all its bonds taken up by those of some other atom or atoms.

Valence is not a constant quantity. It varies in the case of some elements through quite a wide range, the variation depending upon temperature, etc.

EXP. 8. HYDROGEN FROM A METAL AND AN ACID. Many metals when brought in contact with an acid will replace the hydrogen which is the common constituent of all acids. By use of this principle we have a very good method for making the gas, using zinc, (Zn) and sulfuric acid, (H_2SO_4).

Preparation.—Make a gas generator from a wide mouthed bottle thus: Select a cork to fit the bottle snugly and bore two holes of a size to fit the funnel tube (A) and the delivery tube (B). (Bend glass by heating in the broad gas flame used for il-

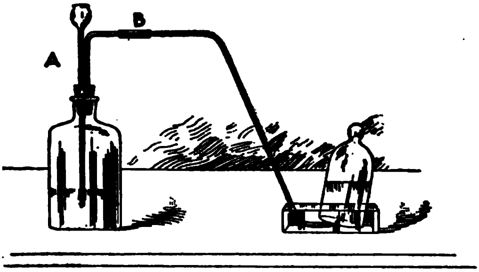


FIG. 2.

luminating.) Take care that the funnel tube and delivery tube fit exactly.

Now put in the bottle enough granulated zinc (Zn) to cover the bottom, and through the funnel pour about 50 *cc** water then add 5 cc. of concentrated sulfuric acid. The zinc will soon begin to dissolve and the hydrogen to be set free. When the action ceases it may again be started by adding another 5 cc. of acid.

An evolution of gas at once begins and it may be collected thus: Fill a bottle or bell-jar full of water and cover with a glass slip, then invert it in a vessel containing water. (Fig. 2.) On removing the glass slip, the jar remains full. Conduct the gas through the delivery tube into this jar and the water will be displaced by the gas. In this way collect several jars of gas and after covering with glass slips set them aside for future use. This process is called "collection by displacement of water" or "collection over water."

Reaction.—Sulfuric acid is a compound of three elements; hydrogen, sulfur and oxygen, and to it is given the formula H_2SO_4. The zinc simply replaces the hydrogen in the acid forming a substance called zinc sulfate ($ZnSO_4$). The hydrogen is set free.

NOTE.—Bottles with wide mouths may be used instead of bell-jars.

* cc. means cubic centimeter.

Represented in chemical formulas the reaction would be written as follows: $Zn+H_2SO_4=ZnSO_4+H_2$.

b.—Filter a small quantity of the liquid left in the generator and evaporate to dryness in a porcelain dish. Note the appearance of the zinc sulfate. This is a typical substance of a class called salts.

Definition.—A *salt* is a compound made by replacing the hydrogen of an acid with a metal. Salts are usually divided into two classes, *normal* and *acid*.

A *normal salt* is one which has been made by replacing all the hydrogen of an acid with a metal. Such a salt is normal sodium sulfate, (Na_2SO_4). Here all the hydrogen atoms of the acid have been replaced by sodium. An acid like sulfuric which contains more than one replaceable atom of hydrogen is known as a polybasic acid. If it contains but two atoms it is said to be dibasic; if three, is called tribasic, etc.

Acid salts result when but part of the hydrogen is replaced, as acid sodium sulfate ($NaHSO_4$).

When a acid contains three replaceable atoms of hydrogen, the salts made from it are named *primary*, *secondary* and *tertiary* according as one, two or three atoms have been replaced. Such are *primary* sodium phosphate (NaH_2PO_4), *secondary* (Na_2HPO_4) and *tertiary* sodium phosphate (Na_3PO_4).

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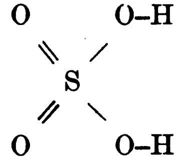
EMPIRICAL AND CONSTITUTIONAL FORMULAS.

We have seen that a formula is the expression used to designate a chemical compound and is made by combining in the proper proportions the symbols of the elements of which the compound is composed. We may write formulas in two ways. We may repeat the symbols of the elements as many times as they occur or place after the symbol an index number which will indicate the number of times it should be written.

The first kind is called a constitutional and the second an *empirical* formula. The constitutional is much used to express complicated compounds such as occur in Organic Chemistry. Such a formula shows the manner in which the atoms are believed to combine. The constitutional formula of sulfuric acid for example is



The empirical formula merely shows the kind and number of atoms in a compound. Sulfuric acid would be written H_2SO_4.

EXP. 9. HYDROGEN FROM WATER BY ELECTROLYSIS.

1. Crack off the bottom of a medium sized, wide mouthed bottle or glass jar. (This may be

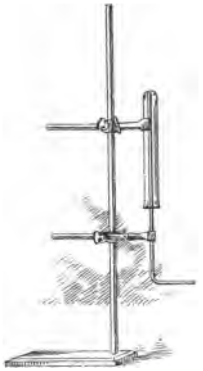
done by scratching the glass with a file, then touching the crack with a red hot glass rod or hot piece of iron. The bottle will break parallel to the file mark.) Close the neck with a close fitting cork, through which two platinum wires pass. Put tips on these wires of small pieces of platinum foil about one-half inch in length by one-quarter wide. Invert the apparatus thus made, support it in some way and fill two-thirds full of water; add two or three cc. of H_2SO_4 and connect the outer ends of the platinum wires with two potassium dichromate or other good cells. Over the platinum tips invert two graduated tubes filled with water. After connecting with the cells bubbles of gas will form on the platinum tips and rise in the tubes. After several cubic centimeters of gas have collected note the ratio between the quantities of gas in the two tubes. In which tube is the hydrogen? What is its quantity relative to the other gas? How do the two gases act with respect to a flame? We have here a new gas which is an active supporter of combustion. It is the oxygen of which we have already spoken.

NOTE—A special form of apparatus made for the decomposition of water is shown in figure, Exp. 28.

Reaction.—Water subjected to the action of the electric current is decomposed into its two constituent gases and these are given off in the exact proportion in which they occur in the compound. Pure water is a nonconductor of electricity but

when slightly acidified it becomes a conductor, hence the use of sulfuric acid.

PROPERTIES OF HYDROGEN.



Exp. 10. Collect one or two jars of the gas by placing the end of the delivery tube in an inverted jar, as in the figure. Such a process is called "collection by upward displacement." What must be the weight of hydrogen as compared with air to make such a process possible?

Exp. 11. Attach a clay pipe to the generator by means of a rubber tube. Make soap bubbles and set them free. What do they do? Is the gas in them heavier than the air? Blow some bubbles from the lungs and set them free. Note the difference between these and those filled with hydrogen. Ignite some hydrogen bubbles when they are some distance away from the generator. Now collect a testtubeful of gas by displacement of water and ignite. Does the hydrogen explode? If it does there is still air mixed with the gas. Allow the gas to generate for a minute or two and test again. When the hydrogen is perfectly free from air perform experiment 12.

NOTE—To make soapsuds use good Castile soap and distilled water. Cut the soap into thin shavings and shake with the warm water. Use while fresh.

Exp. 12. Replace the delivery tube with a jet tube, i. e., a glass tube drawn out to a fine point. If you are sure that no air is present light the jet of gas. *Be very careful in this experiment so that dangerous explosions may be avoided.* A mixture of air and hydrogen is very explosive.

Exp. 13. Over the burning jet hold a clean dry bottle. What is deposited on the sides of bottle? Where does the oxygen come from?

Exp. 14. Thrust a burning taper or splinter into a jar of the gas. Will the gas burn? Will it support combustion? Note the color of the flame. After burning some time the flame may be colored yellow. This is due to sodium which is one of the constituents of the glass.

Exp. 15. Invert an empty jar and invert another filled with hydrogen under it. Test the gas in each jar. What change has taken place? What other experiments show the same properties of the gas?

Exp. 16. HYDROGEN AND OXYGEN.

These two gases combine with great force to form water. The mixture of the gases in the proportion of one part by volume of oxygen to two parts of hydrogen is very explosive. The properties of this mixture can be well shown by the apparatus known as the "hydrogen gun." To make such a gun, punch a hole in the bottom of a small tin can such as a baking powder can. Plug

the vent thus made and fill the can with water. Next displace the water with hydrogen from a generator. When the can is full, bubbles of gas will come out around the mouth. Remove from the water, keeping the can mouth down, remove the plug and apply a light to the vent.

Repeat the experiment, filling the can half full of water. On displacing this with gas the can will be half filled with hydrogen and half with air. Air is a mixture of oxygen with another gas called *nitrogen* and may be used instead of pure oxygen.

OXYGEN.

Symbol O. Atomic weight 16.

Discovered by Priestley in 1774.

The name comes from the Greek and means "an acid maker." Oxygen is so named because the oxygen compounds of the non-metals combine with water to form acids.

Equivalent weights.

We have already learned that elements can replace one another in compounds. For example if we treat a piece of zinc with hydrochloric acid, zinc chlorid ($ZnCl_2$) will be formed and hydrogen will be set free. We may easily prove by experiment that 32.5 parts of zinc are always required to set free one part by weight of hydrogen. In the same way if sodium is thrown into water, for every gram of hydrogen set free 23 grams of sodium are required. It may be proved that whenever one

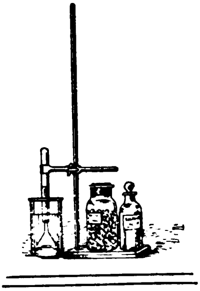
element can replace another there is always a definite weight relation between the elements. Thus we may formulate

THE LAW OF EQUIVALENT WEIGHTS.

When one element takes the place of another in a compound the substitution always takes place in definite proportions. The relative quantities which thus replace one another are called *chemical equivalents*, and are usually identical with, or multiples of, the atomic weights. Hence the determination of equivalent weights is often necessary for a knowledge of the atomic weights of an element.

Problem 1.

Determination of the weight of hydrogen set free by a given weight of zinc.



Weigh very carefully a small piece of zinc. Not more than .02 grams. Place under a funnel in a beaker of water as in the figure. Invert over the funnel a test tube filled with dilute sulfuric acid. Hydrogen will be set free and will collect in the tube. After the zinc is all dissolved raise the tube in the beaker so that the level of the liquid inside and outside is the same and carefully mark the place. Remove the tube from the beaker and fill with water just to the mark then measure the water by pouring it into a graduate. The amount of water will repre-

sent the amount of gas set free. Note the temperature of the water and the height of the barometer. Knowing the volume of the hydrogen, it is an easy matter to determine its weight, since at 0° and 760 mm. pressure 1 cc. weighs .0000896 grams. But our volume is read at a temperature higher than 0° and the pressure is probably not 760. To reduce the volume to the ideal conditions apply the following formula.

$$Vo = \frac{VP}{760\,(1 + a\,t)}.$$

Where V is the volume at the temperature read.

P is the barometer reading at the time of the experiment.

a is .003665.

t is the temperature of the water used in the experiment.

Then the weight of hydrogen set free is

$W = V_0 \times 0000896$.

The weight of 1 cc. of hydrogen at the ideal conditions of temperature and pressure is called a *crith.*

To calculate the amount of zinc necessary to set free one gram of hydrogen apply the following proportion,

Weight of hydrogen : weight of zinc : :1 : x where x is the equivalent weight of zinc.

Problem 2.

In the same manner determine the equivalent weight of magnesium.

Problem 3.

How much zinc and sulfuric acid would be necessary to set free 50 grams of hydrogen?

Explanation. This reaction takes place between the acid and the metal, $Zn+H_2SO_4=ZnSO_4+H_2$.

This means that 1 molecule of zinc will set free 1 molecule hydrogen or as the symbols of the elements represent their atomic weights, 63 parts by weight of zinc will set free 2 parts by weight of hydrogen or for every part of hydrogen 32.5 parts of Zn are necessary.

Therefore to determine the amount of Zn needed to free 50 grams of H apply the following proportion.

63 : 2 :: x : 50. Where x is the weight of Zn.

In other words the molecular weights of Zn and H are to each other as the actual weights in which they combine or replace one another.

Problem 4.

How many cubic-centimeters of hydrogen, at 0° temperature and 760 m. m. barometer pressure, can be obtained from 10 grams of sodium?

Problem 5.

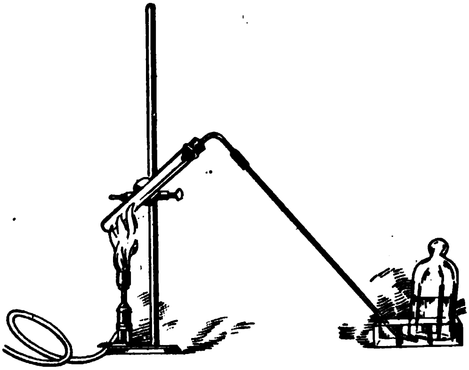
If 15.2 grams of hydrogen are set free by .015 grams of magnesium at a temperature of 20° C and a pressure of 750 mm., what is the equivalent weight of the metal?

PREPARATION.

Exp. 17. Oxygen from mercuric oxid (HgO.) Mercuric oxid is a substance that decomposes

very easily into its constituents, oxygen and mercury.

Fit a test tube of hard glass with a cork and delivery tube. Place in the tube a small quantity of mercuric oxid and heat. Collect the gas which is generated, by displacement of water as in the case of hydrogen.



Note the sublimate in the tube. What is it?

Will the gas burn or support combustion? It may be best tested to see if it will support combustion by thrusting into it a splint on which there is a spark of fire. What is the element in the air that supports combustion?

The reaction in this case is very simple. The mercuric oxid on being heated simply decomposes into its two constituents. HgO heated$=O+Hg$. This is the experiment by which oxygen was discovered.

EXP. 18. OXYGEN FROM MANGANESE DIOXID, (MnO_2).

Repeat the above experiment using manganese dioxid instead of mercuric oxid. Is a sublimate left in the tube?

Reaction.—The manganese dioxid on being heated forms a compound called red oxid of manganese (Mn_3O_4) and oxygen.

$3MnO_2$ heated$=Mn_3O_4+2O$.

Both of the above methods are very unsatisfactory, the first because of the expense of the material and the second because of the high temperature necessary.

EXP. 19. (a) OXYGEN FROM POTASSIUM CHLORATE, ($KClO_3$).

Repeat the above experiment using a small quantity of potassium chlorate. In heating be careful that none of the salt boils out and strikes the hands. It is best to begin to heat at the top of the salt and heat toward the bottom.

After the evolution of gas has ceased, cool the contents of the tube, then dissolve in warm water. Evaporate the solution to dryness and note crystal form, taste and color of the residue. Compare with a sample of potassium chlorate. Is it the same?

Reaction.—This takes place in two stages. First the potassium chlorate at a temperature a little higher than the melting point of the salt

forms a substance called potassium perchlorate, potassium chlorid and a small quantity of oxygen. At a higher temperature this perchlorate decomposes into potassium chlorid and oxygen.

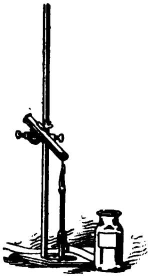
a. $2KClO_3$ heated$=KCl$ (potassium chlorid) $+KClO_4$ (potassium perchlorate) $+2O$.

b. $KClO_4$ heated$=KCl+4O$.

Or the total reaction may be represented by one equation that does not show the intermediate steps, i. e., $KClO_3=KCl+3O$.

To make oxygen from potassium chlorate a comparatively high temperature is necessary. It is a curious fact that if a small quantity of manganese dioxid is added to the chlorate the oxygen will be set free at a lower temperature. The reaction is the same as in the above experiment. The manganese dioxid suffers no change.

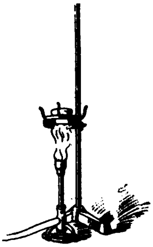
To prove this, melt carefully a small quantity of potassium chlorate in a crucible or test tube. Test to see if any oxygen is given off. Next add a small quantity of manganese dioxid. Is the evolution of gas increased?



Exp. 19. (b) TO DETERMINE THE AMOUNT OF OXYGEN SET FREE FROM A KNOWN WEIGHT OF POTASSIUM CHLORATE.

Weigh carefully a small porcelain crucible. In it place a small quantity of pulverized potassium chlorate and weigh again. The difference is the

weight of the chlorate. It is best to use about one gram of chlorate.



Heat crucible and contents until no gas is given off. Cool and weigh again. The loss represents the weight of oxygen. The difference between the weight of the empty crucible and the crucible plus the residue is the weight of the potassium chlorid.

$KClO_3$ heated$=KCl+3O$.

122 parts by weight of $KClO_3$ will give, on heating, 74 parts of KCl and 48 parts of oxygen.

i. e. $122=K(39)+Cl(35)+3O(3\times16=48)$.
$74=K(39)+Cl(35)$.
$48=3\times O(3O)$.

Supposing we have taken 5 grams of $KClO_3$ for our experiment, then the ratio between 5 g. and the number of grams of KCl formed is the same as that between 122 and 74. Let x equal the weight of KCl which should be formed from 5 g. $KClO_3$, then $5:x::122:74$. Solving we find that this is 3.033 grams. Likewise to determine the amount of oxygen formed from 5 g. $KClO_3$, let y be the amount of oxygen, then $5:y::122:48$. y equals 1.967. $x+y=3.033+1.967=5$.

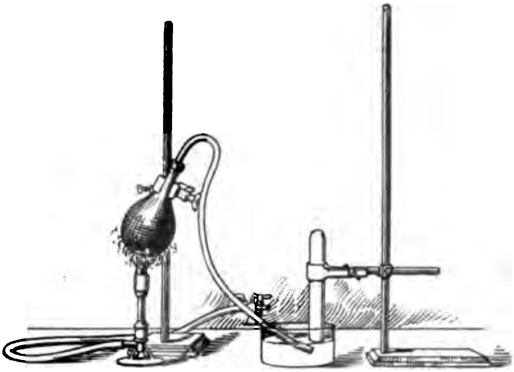
Work out these proportions substituting the number of grams of $KClO_3$ that you used and the amounts of oxygen and KCl obtained.

EXP. 20. OXYGEN FROM POTASSIUM CHLORATE AND MANGANESE DIOXID.

Mix well about 10 grams of $KClO_3$ with one

gram of manganese dioxid and heat in a test tube or flask arranged with cork stopper and delivery tube. Collect several jars of the gas over water and set aside for future experiments.

NOTE—For the preparation of oxygen in large quantities it is best to use a flask of copper.

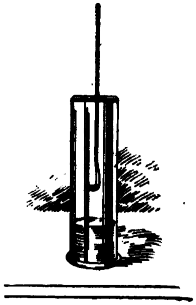


PROPERTIES OF OXYGEN.

EXP. 21. Into a small bottle of oxygen thrust a glowing splint. If it relights, extinguish and relight as often as possible. Will oxygen burn? Will it support combustion?

EXP. 22. Make a deflagrating spoon by hollowing out a piece of crayon or electric light carbon with a knife. Make a handle by wrapping a piece of wire about the chalk. In the deflagrating spoon place a little piece of sulfur and ignite in the Bun-

sen burner and thrust in a bottle of oxygen as in the following figure.



Note the color of the flame and the color of product formed.

Pour a few drops of water into the bottle in which the sulfur has been burned. Test with red and blue litmus paper. What is the action of the liquid on the paper?

An acid has been formed. For definition of acid see p. 17.

Reaction.—The sulfur has combined with the oxygen, forming a gas called sulfur dioxid, SO_2. This combines with water to form an acid. Such a substance is called an anhydrid. We may, therefore, define an anhydrid as a substance which when brought in contact with water will form an acid.

The acid formed in this case is called sulfurous acid and has the formula H_2SO_3. H_2O+SO_2.

Exp. 23. Place a glowing piece of charcoal in the spoon and lower it into a bottle of oxygen. Carbon dioxid is formed according to the equation $C + 2\ O = CO_2$. Pour a few drops of water into the bottle and test as before. Is there any action on litmus? A very weak acid has been made, called carbonic acid. To test for carbonic acid pour a few drops of a solution of calcium hydroxid, $Ca(OH)_2$ into the bottle and shake. A white substance called calcium carbonate is formed having the formula $CaCO_3$.

Exp. 24. Dry a piece of phosphorus as large as an apple seed carefully on blotting paper and place in a deflagrating spoon. Lower into a jar of oxygen and ignite with a warm wire. There should be about half an inch of water in the jar to prevent it from breaking in case some of the burning phosphorus should fall on the bottom.

After the combustion is finished test the water with litmus and carefully taste. Here we have another acid. The phosphorous and oxygen have combined to form P_2O_5. called phosphorous pentoxid or phosphoric anhydrid which with water forms phosphoric acid (H_3PO_4.)

$$P_2O_5+3H_2O=2H_3PO_4.$$

Phosphoric acid is a tribasic acid and forms three classes of salts called primary, secondary and tertiary according as one, two or three of the hydrogen atoms of the acid have been replaced by a metal.

Caution. Phosphorous is a very dangerous substance because of the ease with which it takes fire. For this reason it is always kept under water. It should *never* be handled with the fingers but always with a pair of tongs.

Exp. 25.

Many substances which are incombustible under ordinary conditions burn easily in oxygen. Coil a fine iron wire in the form of a spiral. Warm one end and dip in sulfur. Ignite and thrust in a

jar of oxygen. The iron takes fire and burns brilliantly. It is always necessary to have about an inch of water in the bottom of the jar. Why?

OZONE.

Symbol O_3. Molecular weight 47.64.

Discovered by Schoenbein in 1840.

The name comes from the Greek and means "to smell". So named because of its strong odor.

Ozone is a substance that much resembles ordinary oxygen in its properties. It is a so-called "allotropic" form of oxygen. Certain elements are capable of existing in several different forms. Such are said to have allotropic forms. Allotropic comes from the Greek and means "another".

Ozone is supposed to be the same as oxygen except that it consists of three atoms to the molecule while oxygen has but two. It is easily decomposed and breaks up into a molecule of oxygen O_2 and an atom of oxygen. The atom of oxygen has the same properties as the molecular oxygen except in a much greater degree. The properties of ozone are the same as those of the atomic oxygen and it is believed that these are due to this decomposition. When an element is capable of decomposing into one or more atoms, just after the change has taken place it is said to be in the *nascent state.* Nascent means "just born". In this condition the elements show their properties in a much greater degree than is usual.

Ozone may be made in a number of ways. Its properties are so much like those of oxygen that the student will gain little by making it in the laboratory.

In nature it is generated by the passage of electric flashes through the air. In a similar manner it may be made in the laboratory by means of the electric machine or by passing a silent discharge of electricity through dry oxygen.

The odor may be noted by standing near an electric machine in motion.

COMPOUNDS OF OXYGEN AND HYDROGEN.

There are two such compounds, water, (H_2O) and a much less common substance called hydrogen dioxid, (H_2O_2). The latter has a very limited use in medicine, for bleaching the hair and for cleaning old paintings. It is known in medicine as dioxogen.

WATER.

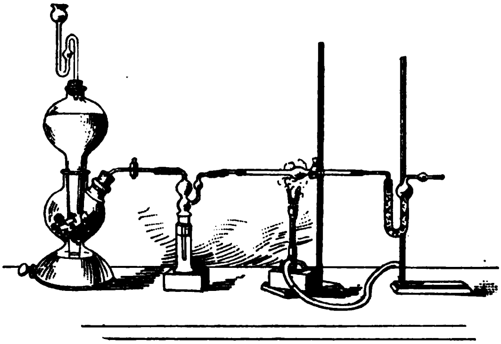
Formula H_2O. Molecular weight 18.

Exp. 26. Burn a jet of hydrogen in the air. Hold a cold dry bottle over the jet. See Exp. 13. All substances which contain hydrogen, on burning, form water. Organic matter, i. e. the product of animal and vegetable life, contains hydrogen thus such matter will form water when burned. To prove this, burn a piece of paper or wood in a clean dry bottle. Note the deposit of moisture on the sides of the bottle.

Breathe on a dry glass plate. Note the moisture. Water is formed in the body by a process analogous to combustion.

Exp. 27. Water prepared from copper oxid (CuO) and hydrogen.

In a bulb of hard glass arranged as in the figure place a weighed quantity of copper oxid. Pass dry hydrogen over the oxid while heating to as high a temperature as possible. The water may be collected in a U formed tube filled with calcium chlorid ($CaCl_2$) which may be weighed before and after the experiment to determine the quantity of water formed. The hydrogen may be dried by passing it through a wash bottle containing concentrated sulfuric acid. See figure.



A is the wash bottle to dry the hydrogen. B is a tube filled with copper oxid. C is the tube filled with $CaCl_2$ to absorb the water.

After the experiment is finished note that the

black copper oxid has changed to a bright color. It has been changed to metallic copper. A process like this where oxygen is taken away from a substance is called *reduction*, while that of adding oxygen is called oxidation. One process is the complement of the other. Which substance has been oxidized in the above experiment?

Reaction,—$CuO+H_2=H_2O+Cu$. This means that 79 parts by weight of CuO with 2 parts of hydrogen will form 18 parts of water and 63 parts of copper, or that 4.39 parts of CuO will form 1 part of water. Thus for every gram of water 4.39 grams of CuO must be changed into copper. Did this hold true in your experiments?

ANALYSIS AND SYNTHESIS OF WATER.

How much water can be prepared from 100g CuO? What weight of H. would be required? What volume would this H. occupy at 20° and 735 mm pressure?

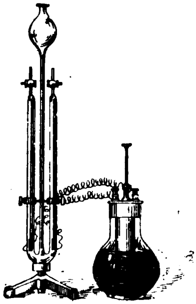
To determine the constitution of any substance we must subject it to a process called *analysis.* If we simply determine what substances are present the process is called *qualitative analysis.* If we determine the quantity of the substances the process is called *quantitative analysis.*

We may also determine the nature of a substance by putting together its constituents and causing them to combine. Such a process is called

synthesis. A synthesis is the opposite of an analysis. Just as we have quantitive and qualitative analysis we may have *quantitative* and *qualitative synthesis.* Both of these processes are well illustrated by the two following experiments.

Exp. 28. Analysis of water.

Repeat Exp. 9. Does the oxygen come off at the + or — pole? One of the distinguishing characteristics of the metals and non-metals is their behavior toward an electric current. When a compound is dissociated by the current, the metal is set free at the — pole and the non-metal at the +.



SYNTHESIS OF WATER.

It has been shown that water can be decomposed into two constituents, oxygen and hydrogen, and that there are exactly two volumes of hydrogen set free for one of oxygen. In like manner we may prove the composition of water by mixing these gases in the proper proportions and exploding the mixture. The two gases will combine completely. This experiment is not well adapted to the use of students but should be shown by the teacher.

WATER OF CRYSTALLIZATION.

Water often occurs combined in salts. In many salts it is essential to the crystal form and is

called water of crystallization.

Exp. 29. Examine some crystals of copper sulfate, ($CuSO_4$). Note the form, color, etc. Heat in a test tube and again examine. What is given off?

Cool and add a small quantity of water. Evaporate the solution to dryness on a water bath. Compare the crystals with those originally used.

Exp. 30. In each of two watch glasses place crystals of sodium carbonate (Na_2CO_3) and sodium sulfate (Na_2SO_4). Allow to stand over night and again observe. What has occured?

Crystals which suffer such a change on being exposed to the air are said to *effloresce* and the phenomonen is named *efflorescence*,

Exp. 31. Repeat the above using calcium chlorid ($CaCl_2$). This salt shows a change which is the opposite of that of two salts used above. This change is called *deliquescence.*

Exp. 32. Heat some crystals of common salt in a test tube. What is given off? Note the crackling sound. This is called *decrepitation.* It is caused by water mechanically enclosed in the crystals.

SOLUTION.

When a solid and a liquid are brought together the solid will often disappear, forming a liquid which looks much like the original. For example if we place a small quantity of common salt in water it will disappear and the water will appear

just as it did before the salt was added. Such a process is called solution. The liquid is called a solvent. Besides solids, liquids and gases will dissolve in liquids. If a liquid which contains a dissolved solid is boiled the solid will usually separate in its original form. Most solids appear in the crystalline form.

A dissolved liquid can usually be separated from its solvent by boiling. The separation is difficult or impossible if the temperatures at which the two liquids are changed to the vapor form are near together. The temperature at which a liquid changes to the vapor form or at which the liquid boils is called the boiling point. All liquids have a definite boiling point which is constant for like conditions of pressure.

Gases may also be separated from their solvent by boiling. The separation usually takes place at a temperature much lower than the boiling point of the solvent. A few gases show an exception to this rule.

Water is an almost universal solvent. It dissolves nearly all known substances in greater or less degree.

Solutions differ from chemical compounds in that they have no definite composition which is the characteristic common to all true chemical compounds. The whole subject of solutions and their properties is but imperfectly understood.

Exp. 33. Determine the temperature of twenty cc. distilled water. Add a quantity of common salt, stir and again note the temperature. Try the same with sodium nitrate ($NaNO_3$) copper sulfate, etc.

If we should attempt to change a quantity of common salt into the form of a powder it would be necessary to do work upon it, i. e. to expend energy. In the same way when a salt is dissolved in water energy is required. The only source of energy in the water is heat so the salt absorbs this heat in changing from the solid to the liquid form. This explains the lowering of the temperature.

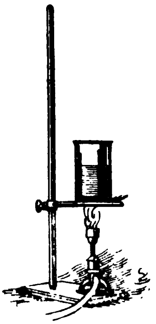
Exp. 34. To a small quantity of water in a test tube gradually add concentrated sulfuric acid and note changes in temperature. Do you see why we should be careful in diluting concentrated sulfuric acid?

In a small quantity of water in an evaporating dish place a small piece of potassium or sodium hydroxid, determining the temperature change.

If a new chemical compound is formed when a solid is dissolved in a solvent, heat will be evolved. For example in the case of the sulfuric acid it is believed that a dilute acid of definite composition is formed i. e. $H_2SO_4 + xH_2O$. This accounts for the rise in temperature in the last experiment.

SOLUTION OF GASES IN WATER.

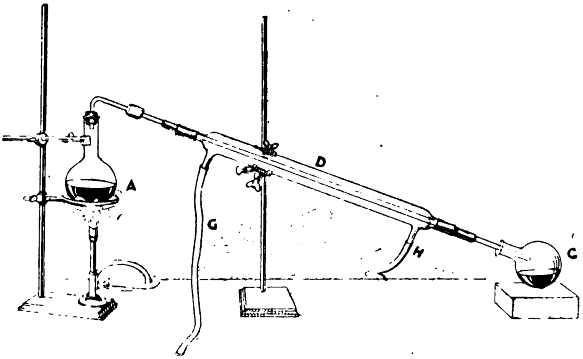
Exp. 35. Place a beaker half full of water on a wire gauze arranged so that it may be heated. Note the temperature at which bubbles of gas are set free. This is a temperature far below the boiling point of water i. e. 100 degrees.



The gases are those ordinarily dissolved in water i. e. the gases of the atmosphere, oxygen and nitrogen.

DISTILLATION.

Water may be freed from most dissolved solids and liquids by the process known as distillation. This is a process by which a substance is changed into vapor, this vapor being again condensed.



Exp. 36. In a distilling flask arranged with a condenser as in the figure, place a solution of 2 grams copper sulfate in 50 cc. water.

Heat the flask until about half the contents have passed over. The liquid that passes over is called the distillate. Evaporate the distillate to dryness and examine. Do the same with the contents of the flask.

A is the distilling flask, D the condenser, C the receiver and H G the tubes by which water is carried through the condenser. During the distillation the condenser should be filled with running water.

THE HALOGEN FAMILY OF ELEMENTS.

Certain elements have so many common or similar properties that they are placed together in groups or families. Such a group is usually named from the most important element or from some characteristic common to all the elements of the group.

The halogen group consists of four elements viz. fluorin, F, atomic weight 18.9; chlorin, Cl, at. wt. 35.19; bromin, Br, 79.36; and iodin, I, 125.91. These have been named in the order of their chemical activity. Fluorin is the most active element of the group, in fact it is the most active element known, forming compounds with nearly all substances oxygen alone excepted. Chlorin is also a very active element but less so than fluorin. Bromin is less active than chlorin, etc. The chemical and physical properties all vary with the atomic weights. Fluorin and chlorin are gases, bromin a

liquid and iodin, of still higher atomic weight, is a solid. Fluorin is least like a metal, i. e., is most non-metallic, while iodin has a few properties like those of the metals. The properties of chlorin and bromin vary between those of the other two halogens.

The name *halogen* comes from the Greek and means a "salt builder" from the fact that all the elements of this group combine directly with the metals to form salts.

FLUORIN.

Symbol F. Atomic weight, 18.9.

Discovered in 1886 by a French chemist, M. Moissan.

The name comes from "*fluo*", I flow. The element was so named because it was first made from fluorite, a substance much used as a flux in smelting operations.

The element fluorin is so active chemically that it can be made only with the greatest difficulty. Its preparation is therefore quite impossible for the beginner.

Fluorin may be best studied in the form of its compound with hydrogen, hydrofluoric acid.

HYDROFLUORIC ACID.

Symbol HF. Molecular weight, 19.9.

Hydrofluoric acid is a very volatile liquid having a low boiling point. It is extremely corrosive

and very dangerous to life if inhaled, so all work with it must be done under a hood, i. e., an apparatus so arranged that all poisonous gases are carried away. If the acid is spilled on the skin it gives rise to very painful and slow healing sores.

Preparation.

The acid may be best prepared from a compound of fluorin with the metal calcium, calcium fluorid, (CaF_2.) By treating this with concentrated sulfuric acid hydrofluoric acid will be formed. The most characteristic property of the acid is its power to etch glass and this may be shown at the same time as its preparation in the following experiment.

Exp. 36. Cover a glass slip on one side with wax or paraffin. Cut with a pin or sharp instrument some design that you wish engraved. Next in a leaden dish under a hood place about four grams of calcium fluorid and add strong sulfuric acid until the fluorid is covered. Warm very gently and cover the dish with the piece of glass with the waxed side down. Allow to stand over night then scrape off the wax and examine. The design that you have drawn will be etched on the glass.

Reaction, $CaF_2 + H_2SO_4 = 2HF + CaSO_4$, calcium sulfate.

Exp. 37. Test the hydrofluoric acid in the leaden dish by holding red litmus paper in it. Do

not put the paper in the liquid but hold just over its surface.

Because of its great chemical activity hydrofluoric acid must be kept in bottles of paraffin, platinum or rubber. These materials are not attacked.

CHLORIN.

Symbol Cl. Atomic weight 35.19.

Discovered by the Swedish chemist Scheele in 1774.

The name comes from the Greek, meaning "of a yellowish green color".

Preparation.

Exp. 38. To a small quantity of manganese dioxid in a test tube add 5-6 cc. of hydrochloric acid, (HCl). Heat the mixture gently. Note the color and odor of the escaping gas.

Perform all experiments with chlorin under a hood as the gas is very irritating to the lungs if breathed.

Add about 10 cc. water to the contents of the test tube and filter. Evaporate the liquid, which is called the filtrate, to dryness in a small porcelain dish and note the formation of crystals.

Bend a small loop in a platinum wire, heat in a flame and while hot dip into a bottle of borax. Heat again until the borax melts into a clear bead. On this bead place a very small quantity of manganese dioxid and heat again. Note that the bead becomes a beautiful amethyst color. This is a characteristic test for manganese and its compounds. Test several different salts of manganese to see that they all give the same reaction with borax.

To a small quantity of hydrochloric acid add a few drops of a solution of silver nitrate, ($AgNO_3$). Note the white solid formed in the tube. This is silver chlorid and is formed with any salt of hydrochloric acid, i. e., any chlorid is treated with a soluble silver compound. This then is a very characteristic test for hydrochloric acid and all its salts.

Now test the salt made by evaporation of the liquid from the above experiment with the bead. What is the color of the bead? Dissolve a little of the salt in water and test with silver nitrate. What is the salt? How would you name it?

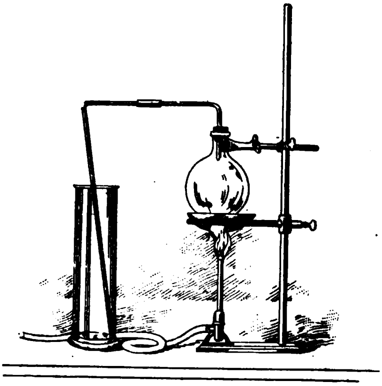
Reaction.

The hydrochloric acid combines with the manganese dioxid, setting free chlorin and forming the salt we have discovered and water. Try to write the reaction.

To make chlorin in quantity.

Hydrochloric acid is made by heating common salt (sodium chlorid) and sulfuric acid together. In making chlorin we may use this reaction instead of ready made acid i. e. mix salt with manganese dioxid and treat the mixture with sulfuric acid.

Exp. 39. Mix one part by weight of manganese dioxid with about two parts of salt and place in a flask fitted with a stopper and delivery tube leading into an upright jar as in the figure. Treat the mixture *with dilute sulfuric acid (1 part water to 2 of acid,) heat and collect several cylinders of the gas. Cover with greased glass slips and set aside for further experiments. When the cylinders are full the yellow chlorin will run over the top.



Gas collected by allowing it to flow into a jar in this way is said to be collected by "downward displacement".

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*Caution.—When concentrated sulfuric acid combines with water great quantities of heat are evolved. Great care must be taken when the two are mixed. *Always* pour the acid into the water. *Never* pour water into the acid. If this caution is not observed very serious accidents may occur because often a sudden evolution of steam may throw hot acid over the experimenter.

Reaction. This takes place in two stages. The first stage is that in which the hydrochloric acid is made.

a. $NaCl + H_2SO_4 = NaHSO_4$ (sodium acid sulfate) $+ HCl$.

b. $MnO_2 + 4HCl = MnCl_2$ (manganese chlorid) $+ 2Cl + 2H_2O$.

PROPERTIES OF CHLORIN.

Exp. 40. Hold a piece of moist blue litmus paper in the gas. Repeat with a moist piece of colored cloth or paper. Repeat same with dry pieces. What takes place in the first case? In the second?

Moist fabric only can be bleached in this manner. The chlorin combines with the hydrogen of the water forming hydrochloric acid, thus setting the oxygen free. When oxygen is first liberated from a compound it is a very active agent combining with and destroying the coloring matter. When an element is first set free from its compounds it is said to be "nascent" i. e. just born. Elements in this state usually exhibit their ordinary properties, but in greater degree.

Reaction. $H_2O + 2Cl = 2HCl + O$.

Exp. 41. Note carefully the odor of chlorin. Is the gas lighter than air? Try to pour some gas from one tube into another.

Invert a cylinder of Cl in water. What happens? What do you now know about the solubility of chlorin in water?

Exp. 42. Lower a lighted taper into a jar of chlorin. Does the gas burn or support combustion?

CHLORIN AND METALS.

Chlorin has a great affinity for metals. In the nascent state it will combine with nearly all of them.

Exp. 43. Pulverize some metallic antimony (Sb). Throw a small quantity of the powder into a tall jar containing chlorin. A compound of antimony and chlorin is formed, antimony trichlorid ($SbCl_3$).

CHLORIN AND HYDROGEN.

Chlorin forms one compound with hydrogen. This is hydrochloric acid (HCl) one of the most important acids known to science.

HYDROCHLORIC ACID.

Formula. HCl. Molecular weight 36.19.

Exp. 44. In a jar of chlorin burn a jet of hydrogen. Continue until the yellow green color of the chlorin has disappeared. Note the liquid forming on the sides of the jar. Note odor and taste. Blow across the top of the jar. Note that the liquid fumes when the moisture of the breath comes in contact with it.

HYDROCHLORIC ACID FROM SALT AND SULFURIC ACID.

Exp. 45. To about 5 grams of common salt

placed in a flask or large test tube, arranged with a stopper and delivery tube, add 10 cc. dilute sulfuric (2 parts water to 1 part of acid see p. 30). Heat gently and collect the gas by downward displacement as you did chlorin. Collect several jars, cover with glass slips and set aside.

In working with hydrochloric acid it is absolutely necessary that the jars be dry, otherwise the gas is absorbed by the moisture and poor results will be obtained in nearly all the experiments.

Reactions.—The reaction between the salt and the acid takes place in two different ways according as the salt or the acid is in excess.

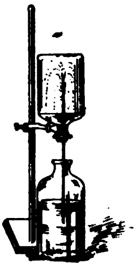
a. Acid in excess. $NaCl + H_2SO_4 = NaHSO_4$ (sodium acid sulfate) $+ HCl$.

b. Salt in excess. $2NaCl + H_2SO_4 = Na_2SO_4$ (normal sodium sulfate) $+ 2HCl$.

PROPERTIES OF HYDROCHLORIC ACID.

Exp. 46. Solubility in water. Select a large dry bottle having a small short neck. Fill with dry hydrochloric acid gas by downward displacement. The bottle is full when a rod dipped in *ammonia* (NH_4OH) held at the mouth will give off dense white fumes. These are fumes of *ammonium chlorid* (NH_4Cl). Close the mouth of the flask with a cork carrying a jet tube with the small end inside. Dip the neck of the bottle into a large beaker or bottle filled with water in which is a small

quantity of blue litmus solution. In a short time the liquid will rush up into the bottle. What is the cause? Why does the litmus change color? Can hydrochloric acid be collected over water? How does the solubility of this acid compare with that of the element chlorin?



Reaction for the formation of ammonium chlorid. $NH_4OH + HCl = NH_4Cl + H_2O$.

Exp. 47. Test a bottle of the gas with blue litmus paper. Test with a burning splint.

Exp. 48. We have already seen that hydrochloric acid is soluble in water. Make a solution by passing the gas into water for several minutes. This is the way in which the commercial acid is made.

To a small portion of this solution add a drop of silver nitrate solution ($AgNO_3$). What happens?

Reaction. $AgNO_3 + HCl = \underset{\text{WHITE}}{\underline{AgCl}}$ (silver chlorid) $+ HNO_3$ (nitric acid).

Try the same with a solution of lead acetate $Pb(C_2H_3O_2)_2$.

Reaction. $Pb(C_2H_3O_2)_2 + 2HCl = \underset{\text{WHITE}}{\underline{PbCl_2}}$ (lead chlorid) $+ 2HC_2H_3O_2$ (acetic acid).

Repeat with mercurous nitrate.

Reaction. $HgNO_3 + HCl = \underset{\text{WHITE}}{\underline{HgCl}}$ (mercurous chlorid) $+ HNO_2$.

NOTE—In all these experiments a single drop will suffice. Never use large quantities of reagents unless so directed.

Repeat experiment 48 with a solution of NaCl in water instead of HCl.

SOLUBILITY OF METALS IN HYDROCHLORIC ACID.

Exp. 49. Dissolve a small quantity of iron filings in the acid from your table. Is a gas given off? Test with a burning splint. What is it? Repeat with Zn.

In a small evaporating dish evaporate these solutions to dryness. Note what you have left from each solution after evaporation. You have two salts, one of iron and one of zinc. Hydrochloric acid dissolves metals to form salts. Not all metals are soluble in hydrochloric acid, though many are. Write all the reactions that are involved.

Exp. 50. Place a very small piece of gold leaf in each of two test tubes. In one pour a few drops of hydrochloric acid solution and in the other an equal quantity of nitric acid (HNO_3). Note the effect. Warm both tubes. Is there any change. Now pour the contents of the two tubes together.

Gold is one of the few metals that hydrochloric acid will not dissolve. If however the acid is decomposed by any agent so that it will give up its chlorin, the nascent chlorin will dissolve the metal. Such an agent is nitric acid (HNO_3). A mixture of nitric and hydrochloric acids is called Aqua Regia, "King of Waters", from the fact that it will will dissolve gold, "The King of Metals".

Reaction. $3HCl + HNO_3 =$ (nitrosyl chlorid) $NOCl + Cl_2 + 2H_2O$.

ANALYSIS OF HYDROCHLORIC ACID.

Exp. 52. Fit a long test tube with a tightly fitting rubber stopper. Fill the tube with hydrochloric acid gas which has been dried by passing it through a wash bottle containing concentrated sulfuric acid (Exp. 27. A.) Drop into the tube a few grams of powdered sodium amalgam, close and shake well. Place the mouth of the tube under water and open. Note the height to which the water will rise. Test the remaining gas with a flame. What is it?

If the experiment has been properly performed there should be just half as much gas in the tube at the close of the experiment as at the beginning. One of the two constituents of the hydrochloric acid has been absorbed by the amalgam.

We see that hydrochloric acid is composed of equal volumes of the two gases hydrogen and chlorin.

This same truth can be proved by a synthetical experiment. By mixing equal volumes of the two gases and then applying a flame to the mixture they will completely combine to form hydrochloric acid. *The synthesis is not well adapted to the use of the student.*

Sodium amalgam. This is a compound of mercury (Hg) and the metal sodium. It may be purchased but is easily prepared if a few precautions are observed. Best prepared by the teacher.

For the amalgam 10 parts by weight of mercury are used for one of sodium. Place the mercury in a crucible under a hood and then put the sodium into it, having first cut the metal into thin slices. The sodium may best be brought into the mercury by means of a glass rod which has been drawn out to a point and bent at right angles. Protect the hands with gloves and the eyes with large glasses. Be sure that the draught in the hood is good.

After cooling, the amalgam may be shaken out of the mortar and pulverized.

LAW OF GAY LUSSAC.

Note in the above experiment that one volume of hydrogen combines with one volume of chlorin to form two volumes of hydrochloric acid gas. Or, vice versa, two volumes of hydrochloric acid gas will decompose into one volume of hydrogen and one of chlorin. In a similar manner two volumes of hydrogen combine with one of oxygen to form two of steam. Many other experiments show that when two gases combine to form a product that may be studied in the gaseous state, their volumes are in a simple ratio to that of the product formed. This is called the Law of Gay Lussac.

THE KINETIC THEORY OF GASES.

A gas is supposed to be a form of matter which is composed of molecules moving about in a

medium which for want of a better name we call the "ether". Gases in their movements exert pressure on the sides and bottoms of the vessels in which they may be contained, this pressure varying with the temperature. The pressure is supposed to be due to the impact of the molecules against the walls. When a gas is heated the velocity of the molecules increases and its pressure increases. Hence a gas has a greater pressure hot than cold.

For example a volume of hydrogen is believed to be composed of a great number of the perfectly elastic hydrogen molecules moving about with great rapidity, striking against the walls of the containing vessel, rebounding and flying in another direction until they strike another wall or other molecules, etc.

The energy due to the movement of the molecule of a gas is known as kinetic energy or energy of motion.

This is known as the Kinetic Theory of gases.

AVOGADRO'S THEORY.

It may be shown by a great number of experiments that gases expand uniformly on being heated. This is sometimes called the Law of Dalton or Charles. Likewise it may be proved that if a gas is confined in a closed space and the pressure is increased it will decrease in vol-

ume uniformly. This is called Boyle's Law.

All gases show these same properties. These properties can be explained if we assume that all gases contain in equal volumes, at like conditions of pressure and temperature, *an equal number of molecules,* This theory was advanced by the Italian physicist Avogadro and receives its name from him.

If this theory is correct and we have every reason to think that it is, we can explain the action of chlorin and hydrogen in combining to form exactly two volumes of hydrochloric acid gas. Many other facts of chemistry become clear that would be almost impossible to explain if any other nature was assigned to gases.

RELATION OF THE WEIGHTS OF EQUAL VOLUMES OF GASES TO THEIR MOLECULAR WEIGHTS.

Since the weight of a volume of a gas is equal to the sum of the weights of the molecules composing it, by comparing the weights of equal volumes of different gases we can determine the relative weights of the molecules composing these gases.

For example suppose we have equal volumes of two different gases under like conditions. These volumes are made up of equal numbers of molecules. Let us say that the number of molecules is equal to n. Let the weights of the molecules in the two stages equal x and y respectively.

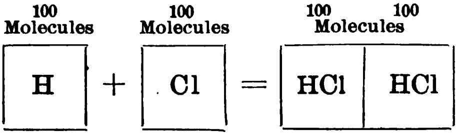
Then nx is the weight of the first gas and ny that of the second. Hence.—nx : ny : : x : y. or the weights of the molecules of the first gas are to those of the second as the weight of a volume of the first is to that of an equal volume of the second.

The weight of a gas as compared with that of some other gas taken as a standard is known as its *specific weight.* Now we may state our law in a new form i. e. *the molecular weights of gases are to each other as the specific weights of those gases.*

Hydrogen is taken as the standard of specific weights for gases because it is the lightest gas known. For common work air may be used instead of hydrogen. Its specific weight in terms of hydrogen has been carefully determined, so it may be taken as a standard.

THE HYDROGEN MOLECULE CONSISTS OF AT LEAST TWO ATOMS.

Molecules, as we have learned, are complex. They consist of more than one atom. The hydrogen molecule consists of two atoms as can be demonstrated in the following manner. Suppose as in the last experiment we combine a volume of hydrogen with one of chlorin. The result is a volume of hydrochloric acid gas equal to the sum of the two volumes of the component gases i. e.



Let us suppose that the volume of hydrogen contains 100 molecules. Each molecule of hydrochloric acid is composed of one atom of H with one of Cl. In each volume of HCl there would of necessity be 100 atoms of H, or 200 atoms in the two volumes. This can only be explained by allowing two atoms for each molecule of hydrogen.

The same course of reasoning may be applied to the volume of chlorin and it may be proved that the chlorin molecule must consist of two atoms.

Again when oxygen and hydrogen combine to form water we know that two volumes of hydrogen and one of oxygen will form two volumes of steam, i. e. water in the gaseous form.

$$\boxed{H_2} + \boxed{H_2} + \boxed{O_2} = \boxed{H_2O \mid H_2O}$$

Each molecule of water is composed of two atoms of hydrogen and one of oxygen so the volumes of these gases must be made up of molecules containing two atoms each.

RELATION OF THE MOLECULAR WEIGHTS OF GASES TO THEIR ATOMIC WEIGHTS.

We have already learned that the atomic weight of an element is the weight of its atom as compared with the weight of an atom of hydrogen. We cannot weigh the atom but we can determine the weights of two equal volumes of gases. From these weights we may determine the atomic

weights. For example, a volume of oxygen is 16 times as heavy as an equal volume of hydrogen at the same temperature and pressure. As the hydrogen molecule contains two atoms the weight of a molecule of oxygen is 2×16=32. The quantity 32 is called the Molecular Weight of oxygen.

In a similar manner it may be shown that the molecular weights of most gases are equal to their specific weights as compared with hydrogen, multiplied by 2.

The weight which we assign to an element as its atomic weight is the least weight that can enter into any of its compounds. We may determine these weights by many different methods using the molecular weight as the starting point. For example, water has a molecular weight of 18. We determine it by comparing a volume of hydrogen with an equal volume of steam, water in the gaseous form. The weight of steam is 9 times that of hydrogen under the same conditions. The molecule weighs 2×9=18. By analysis water may be shown to contain 88.88% of oxygen and 11.11% of hydrogen. If then we calculate the actual parts by weight of the two elements in 18 parts by weight of water, we have the following: 88.88% of 18 is about 16, and 11.11% of 18 is about 2. If we make this calculation in the case of a great number of oxygen compounds of which we know the molecular weights we shall find that the number

16 represents the least weight of oxygen that can enter into combination. This then is the atomic weight of oxygen.

The same method of reasoning may be applied to many other elements and their atomic weights calculated in the same way.

SPECIFIC GRAVITY.

The specific gravity of a substance is its weight as compared with the weight of an equal volume of another substance taken as a unit.

The standard for gases is hydrogen and its specific gravity is 1. To determine the specific gravity of any other gas we have simply to compare the weight of a volume of the gas with that of an equal volume of hydrogen. Although hydrogen is the standard, air is more often used because of the greater convenience, and then, as the ratio of the weight of air to that of hydrogen is known the gas whose specific gravity it is desired to determine can be easily referred to hydrogen.

Water is taken as the standard for liquids and solids. Of these standards hydrogen and water, hydrogen has been chosen because it is the lightest gas known and water because of its convenience. Any other gases or liquids might have been chosen.

When we say that sulfuric acid has a specific gravity of 1.84 we mean that one volume of the acid i. e. 1 cc., 1 liter, 1 cubic foot, etc. weighs

exactly 1.84 times as much as an equal volume of water.

The term specific density or simply density is applied to gases alone and is the weight of a gas compared with that of an equal volume of hydrogen.

PROBLEMS.

1. If 1 liter of Cl weighs 3.136 g. how many liters can be obtained from 1000 g $Mn\ O_2$ and HCl?

2. How much salt (NaCl) would be required to make 50 grams of Cl?

3. What would be the weight of Na_2SO_4 formed in the preparation of 100 liters Cl?

4. What would be the quantity of zinc with which 100 g. HCl would combine if the acid had a purity of 36%?

BROMIN.

Symbol Br. Atomic weight 70.36.

Discovered by Balard in 1826.

The name comes from the Greek and means a "bad smell".

Preparation. Bromin has such a disagreeable odor that it should only be made in small quantities and under a hood.

Exp. 53. Pulverize two or three crystals of potassium bromid, KBr. Mix with an equal amount of manganese dioxid, MnO_2. Place in a test tube then add a mixture of 5 cc. water and 1 cc. of

concentrated sulfuric acid. Warm gently and the bromin will be given off in the form of vapor.

Reaction. This takes place in two stages as in the case of chlorin. Hydrobromic acid is first formed.

a. $KBr + H_2SO_4 = KHSO_4$ (acid potassium sulfate) + HBr (hydrobromic acid).

b. $MnO_2 + 4HBr = MnBr_2$ (manganese bromid) $+ Br_2 + 2H_2O$.

These two reactions take place practically at the same time and a third reaction takes place between the manganese bromid and the sulfuric acid so that the final salt of manganese is manganese sulfate $MnSO_4$.

c. $2KBr + MnO_2 + 3H_2SO_4 = 2KHSO_4 + MnSO_4 + 2H_2O + Br_2$.

Exp. 54. Note the color of the bromin, then carefully its odor. Be careful not to inhale too much. Test the gas with a burning splint. Test as you did chlorin with blue litmus paper or with colored cloth. Is there any similarity in the action toward dyes between chlorin and bromin?

Exp. 55. Cork the tube of Exp. 53, invert and place the mouth of the tube under water. Remove the cork. Is bromin as soluble in water as chlorin?

Exp. 56. Make a little chlorin water by heating a few crystals of potassium chlorate with concentrated hydrochloric acid in a test tube.

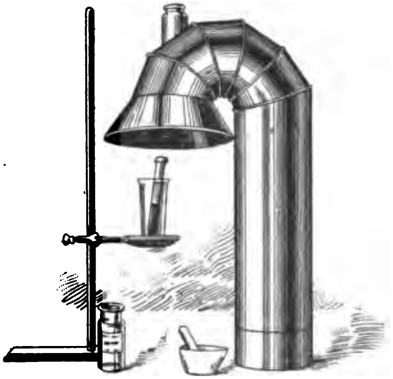
Dissolve a crystal of potassium bromid in water, add a few drops of the chlorin water and note the result. Bromin is set free. To prove this, add one or two drops of carbon disulfid, CS_2, to the solution and shake. When the CS_2 has settled note its color. This is a very common test for bromin.

NOTE—Carbon disulfid is substance very much used in organic chemistry as a solvent.

Reactions. a. To show the formation of chlorin from $KClO_3$ and HCl.

$2KClO_3+4HCl=2KCl$ (potassium chlorid) + $2H_2O+2ClO_2$ (chlorin dioxid) $+Cl_2$.

b. $KBr+Cl=KCl+Br$.



Exp. 57. Starch paste test for bromin. Make a thin starch paste and add a little to a solution containing bromin. Shake well and note the color.

Exp. 58. Action of bromin on metals. *Danger.* Under a hood in good working order, place a test tube containing 2 or 3 drops of bromin. Into this drop a small piece of metallic antimony (Sb). It will burn on the surface of the liquid. Protect the hands with gloves and the eyes with glasses.

BROMIN AND HYDROGEN.

Bromin like chlorin forms but one compound with hydrogen. This is hydrobromic acid HBr.

HYDROBROMIC ACID.

Formula HBr. Molecular weight 80.36.

Exp. 59. Try to make hydrobromic acid as you did hydrochloric using KBr instead of NaCl. Follow Exp. 45.

Over the mouth of the tube hold a rod dipped in ammonia. What is formed? Compare with Exp. 46. Write the reaction. Invert the tube in water. Is hydrogen bromid soluble?

Exp. 60. In a test tube under the hood place a few drops of bromin. Into the tube introduce a burning jet of hydrogen. Note the fuming gas formed. Note odor and action on litmus.

Exp. 61. To a portion of a solution of hydrobromic acid in water, or, what will do just as well, a solution of potassium bromid in water, add a few drops of lead nitrate. To another portion add a few drops of silver nitrate and to another a few drops of mercurous nitrate. Lead bromid, $PbBr_2$,

silver bromid, AgBr, and mercurous bromid, HgBr, are formed. Write the reactions. They are analogous to those in Exp. 48.

IODIN.

Symbol I. Atomic weight 125.91.

Discovered by Courtois in 1811.

The name comes from the Greek meaning "of a violet color".

Preparation.

Exp. 62. Heat together a few crystals of potassium iodid (KI) mixed with manganese dioxid and sulfuric acid as in Exp. 53. It is not necessary to use a hood if the iodin is made in small quantities. Write the reaction. It is analogous to that in Exp. 53.

Exp. 63. Note the color and odor of iodin vapor. Is the vapor heavier or lighter than air? Test with a burning splint, with litmus paper, with colored cloth. How does the bleaching action compare with that of bromin and chlorin? Is iodin a solid, liquid, or gas? Invert the tube in which iodin was made in water. Is iodin soluble in water?

Exp. 64. Make a solution of potassium iodid in water. Add a few drops of chlorin water, add CS_2, shake and note the color. Repeat with a solution of bromin in water instead of chlorin.

Try the above with starch paste instead of CS_2.

IODIN AND METALS.

Exp. 65. Under a hood in a test tube or small crucible heat together a few crystals of iodin and a little mercury. Beautiful crystals of mercuric iodid, HgI_2, will be formed.

Exp. 66. Iodin and phosphorous.

Phosphorous is a substance which combines very readily with iodin. This experiment should be performed under a hood. Carefully dry a small piece of phosphorous not larger than a grain of wheat or apple seed, on blotting paper. Handle with forceps to prevent being burned. Lay the little piece on a board and on it place a crystal of iodin. The phosphorous takes fire.

Reaction. $P + 3I = PI_3$. (phosphorous triiodid.)

Scrape up as much of the PI_3 as possible and save for a later experiment.

Exp. 67. In each of four test tubes place a few crystals of iodin. In one pour a few drops of water, in another, carbon disulfid, in the third, alcohol, C_2H_5OH, and in the last a solution of KBr in water. Shake each tube. Which is the best solvent of iodin?

HYDRIODIC ACID.

Formula HI. Molecular weight 126.91.

Exp. 68. To a small quantity of water add a little PI_3. Hydriodic acid is formed according to the reaction.

$PI_3 + 3H_2O = H_3PO_3$ (phosphorous acid) $+3HI$.

To prove that the HI is present, add a few drops of mercuric chlorid ($HgCl_2$) to the above solution and note the color of the mercuric iodid formed. This is a good test for hydriodic acid and the salts derived from it.

Exp. 69. Hydriodic acid from iodin and hydrogen sulfid (H_2S). Place two or three crystals of iodin in a test tube, add ten cc. water and heat until the iodin goes into solution. Run into the solution hydrogen sulfid gas until the brown color disappears. Boil the solution until it no longer smells of H_2S. We now have a dilute solution of hydriodic acid containing another element, sulfur (S) in the form of a fine powder. This powder will settle after the solution has stood some time or mav be partially removed by filtration.

Exp. 70. To a small quantity of the solution add a little mercuric chlorid, ($HgCl_2$), try another portion with silver nitrate ($AgNO_3$), and a third with lead nitrate $Pb(NO_3)_2$. Write the reactions.

Try same using a solution of KBr in water.

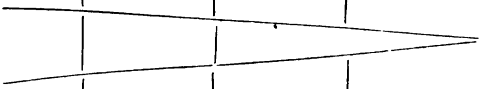
PROBLEMS.

1. What weight of HF can be obtained from 10 g. CaF_2?

2. What weight of KOH would be necessary to neutralize the above amount of HF? How much KF would be formed?

3. What is the percentage of HCl in a solution of which 17 g. will dissolve 2 grams of metallic magnesium? What volume of hydrogen would be liberated in the reaction at 755 mm. pressure and temperature of 30°C?

COMPARISON OF THE ELEMENTS OF THE HALOGEN GROUP.

NAME	Fluorin	Chlorin	Bromin	Iodin
SYMBOL	F	Cl	Br	I
ATOMIC WEIGHT	18.9	35.19	79.36	125.91.
FORM	Gas	Gas	Liquid	Solid.
DISCOVERED	Moissan 1886	Scheele 1774	Balard 1826	Courtois 1811
CHEMICAL ACTIVITY				
COMPOUNDS WITH HYDROGEN	HF	HCl	HBr	HI

COMPARISON OF THE HYDROGEN COMPOUNDS OF THE HALOGEN ELEMENTS.

COMPOUNDS.	HYDROFLUORIC ACID.	HYDROCHLORIC ACID.	HYDROBROMIC ACID.	HYDROIODIC ACID.
Spec. Gravity $H_2 = 2$.	19.91	36.19	80.36	126.91
Molecular Wt.	19.91	36.19	80.36	126.91
Formula.	HF	HCl	HBr	HI
Occurrence.	Never Free	In gases of some volcanoes In Mineral Springs, etc.	In form of salts, especially of K & Na in sea waters & Mnrl. Sprngs	In form of K & Na salts in sea & mineral waters, in ash of sea plnts
Methods of Preparation.	$CaF_2 + H_2SO_4 = 2HF + CaSO_4$	$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl$	$2KBr + H_2SO_4 = K_2SO_4 + 2HBr$	$PI_3 + 3HO_2 = H_3PO_4 + 3HI$
Action on Chlorin.	……	……	Frees Br.	Frees I
Composition by Volume.	1:1	1:1	1:1	1:1
Composition by Weight.	18.9:1	35.19:1	79.36:1	125.91:1
Acid Action on Litmus.				
Action on Metals.				

THE OXYGEN FAMILY.

There are four elements that show the same relationship to one another that the halogens do. These are the common elements oxygen and sulfur and the rarer selenium and tellurium. The last are so much like the former in their properties and in the compounds which they form that no experiments are given. For their relationship to oxygen and sulfur see the table P.

SULFUR.

Symbol S. Atomic weight 31.98.

Sulfur is an element which has been known so long that no date can be given for its discovery.

Sulfur occurs widely distributed in nature both in the free form and in compounds such as sulfates, sulfids etc. It is found free near volcanoes, especially in Sicily. In this country it is found in California, Nevada, Louisiana and other places. In volcanic regions it is also found as hydrogen sulfid, (H_2S) and as sulfur dioxid (SO_2.)

Exp. 71. Examine a piece of roll sulfur, (brimstone.) State as many of its properties as possible. Examine some fine sulfur, precipitated sulfur or flowers of sulfur. Compare with the brimstone.

Exp. 72. Preparation. Sulfur is probably made in volcanic regions by the combination of the two gases H_2S and SO_2. Fill a bottle or bell jar

with sulfur dioxid by burning a small quantity of sulfur in it. Lower the sulfur into the jar with H_2S from a generater. Bring the two together mouth to mouth. Note the precipitate on walls. What is it?

Reaction. $SO_2 + 2H_2S = 2H_2O + 3S$, or when equal parts of the two gases are present.

$5SO_2 + 5H_2S = 4H_2S_5O_6$ pentathionic acid.

The above experiment may be performed in this way. Into a bottle filled with SO_2 lead H_2S from a generator. The S will be deposited as before.

ALLOTROPIC FORMS OF SULFUR.

Sulfur like oxygen exists in several different forms.

Exp. ~~73.~~ Crystalline sulfur. In a small cheap beaker place about 50 grams of roll sulfur and heat to melting. Allow to cool and when a crust forms over the top, break a hole in it and pour the molten sulfur into a beaker of cold water.

Examine the crystals and note form color, etc. Allow to stand for several days and then examine again. What is happening to them?

Examine the sulfur which was poured into water. This is another allotropic form called *amorphous* to distinguish it from the crystalline form. Remove this amorphous sulfur from the water and allow to stand for several days. Again

examine. What seems to be the most general form of sulfur?

Exp. 74. Pulverize a small piece of roll sulfur and shake up with carbon disulfid in a test tube. Pour into a small dish and allow the solvent to evaporate. Note the color and shape of the crystals formed. Keep the CS_2 away from a flame as it takes fire very easily.

SULFUR AND OXYGEN.

Exp. 75. Burn a small quantity of sulfur in a deflagrating spoon in a jar of oxygen or air. Note the color and odor of the gas formed. This gas is a compound of sulfur and oxygen called *sulfur dioxid* having the formula SO_2.

Pour a few drops of water into the jar and shake. Taste the liquid and test with blue litmus paper. What are the properties of the solution? An acid has been formed called *sulfurous acid*, H_2SO_3. Because SO_2 will combine with water to form an acid it is an acid anhydrid.

How many classes of salts can sulfurous acid form? How would they be named?

Exp. 76. In a jar of sulfur dioxid hold a moist colored flower. Try the same with a moist straw. Does the color change in each case? Do you know of any practical application of this principle?

Prepare dilute sulfuric acid by mixing 3 drops

of concentrated sulfuric acid with 3 cc. of water. Dip the bleached flower in this solution. Does the color return?

Reaction. The sulfur in bleaching combines with the oxygen of the water with which the flower is moistened and forms a higher oxid of sulfur, sulfur trioxid (SO_3). Hydrogen is set free and this combines with the coloring matter forming colorless compounds. The SO_3 as soon as formed unites with water forming sulfuric acid (H_2SO_4).

a. $SO_2 + H_2O = SO_3 + H_2$.

b. $SO_3 + H_2O = H_2SO_4$.

As sulfur trioxid will combine with water to form sulfuric acid it is the anhydrid of sulfuric acid. (See page 19.)

The change made by the sulfur dioxid is only temporary. The color may be restored by dipping the material in dilute acids or by exposing it to the air. The coloring matter is not destroyed as in the case of a chlorin bleach. Evidently the hydrogen merely combines with the coloring matter to form a new compound that has no color and the original compound is made again when the fabric is treated with an acid. Or the action may be one of reduction i.e. the hydrogen combines with the oxygen of the coloring substance. Any agent which will readily combine with oxygen is called a *reducing agent* and the process of taking oxygen away from a compound is called *reduction.* On the other hand any substance which will give up oxy-

gen to a compound is an *oxidizing agent* and the process of adding oxygen to a substance is called *oxidation*. Oxidation and reduction are complementary processes. Whenever one occurs the other does also. For example in the above reaction, $H_2O + SO_2 = SO_3 + H_2$. The amount of oxygen combined with the sulfur is changed from two to three atoms hence the SO_2 is oxidized. On the other hand oxygen is taken away from H_2O so H_2O is reduced to H_2. In an earlier example, $CuO + H_2 = H_2O + Cu$, here the CuO is reduced and the H oxidized.

Sulfur and potassium chlorate $KClO_3$.

Sulfur is a very strong reducing agent, that is, it will combine readily with oxygen. If sulfur is brought into contact with a substance which is easily reduced i. e. an oxidizing substance, it will combine with almost explosive violence. A substance which gives up its oxygen very readily is potassium chlorate.

Exp. 77. Pulverize about half a gram of potassium chlorate, mix carefully with an equal quantity of fine sulfur. Divide the mixture into two parts. Place half in a little pile on an anvil or piece of metal and strike with hammer.

SULFUR AND METALS.

Exp. 78. Heat 50 or 60 grams of flowers of of sulfur in a small flask until the sulfur vapors burn at the mouth of the flask. Make a spiral of

fine copper wire by winding it around a pencil or glass tube. Heat to redness and lower into flask where it will burn with a brilliant flame.

Exp. 79. Mix equal quantities of sulfur and fine iron filings and heat gently. The two combine with great energy. Cool and break the tube. Examine the contents.

Reaction. $Fe + S = FeS$ (ferrous sulfid). Save for a later experiment.

Exp. 80. Mix 6 grams of zinc dust with 3 of powdered sulfur. In mixing do not use pressure as this may cause the mixture to explode. Carefully light the mixture using a long taper or splint. Examine the residue. Save the residue for a later experiment.

Reaction. Zn (zinc) $+ S = ZnS$ (zinc sulfid.)

SULFUR AND HYDROGEN.

There are two compounds of hydrogen and sulfur. Sulfur forms a compound analogous to hydrogen dioxid (H_2O_2) called hydrogen disulfid or persulfid. This has the formula H_2S_2. It is an oily yellow liquid having a disagreeable odor. It has little importance.

The other compound called hydrogen sulfid (H_2S) is of great importance especially in analytical chemistry where it is much used to separate certain metals.

HYDROGEN SULFID.

Formula H_2S. Molecular weight 33.82.

Hydrogen sulfid is first mentioned by the Alchemists of the fourth and fifth centuries but was not accurately described until the sixteenth.

Experiments with hydrogen sulfid should be performed under a hood as it is a very disagreeable and poisonous substance.

Preparation.

Exp. 81. a. Treat a little of the ferrous sulfid of Exp. 79 with dilute hydrochloric acid. Note the odor, color, action towards a flame, towards blue litmus paper, etc. In the gas hang a piece of paper moistened in a solution of some salt of lead. Either lead acetate Pb $(C_2H_3O_2)$ or lead nitrats Pb (NO_3) may be used. Note that the paper blackens. This is due to the formation of lead sulfid (PbS) $Pb.(NO_3)_2 + H_3S = PbS + 2HNO_3$ (nitric acid.)

When the hydrogen sulfid burns what is formed? Write the equation. From the action on litmus paper how would you classify hydrogen sulfid?

Reaction for formation of H_2S.

$FeS + 2HCl = {}_2S + H\,FeCl_2$ (ferrous chlorid.)

b. Repeat Exp. 81 using the zinc sulfid made in Exp. 80.

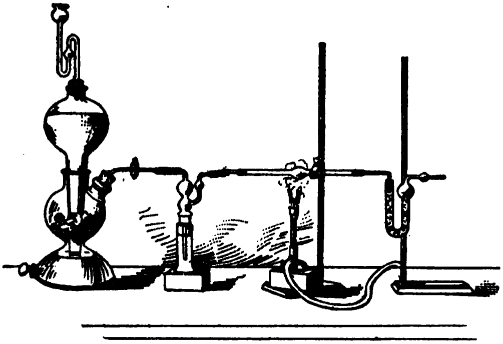
Reaction. $ZnS + 2HCl = H_2S + ZnCl_2$ (zinc chlorid.)

Instead of hydrochloric acid we may use dilute

sulfuric. Write the reactions for sulfuric acid and zinc sulfid; for FeS.

Hydrogen sulfid from its elements sulfur and hydrogen.

Exp. 82. In a bulb of hard glass as shown in the figure, place a small quantity of sulfur and



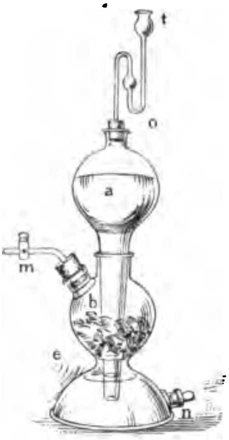
heat. Over the hot sulfur pass a slow stream of hydrogen from a generator. Test the hydrogen first to see that it is free from air.

At the outlet of the bulb tube hang a piece of paper dipped in lead acetate solution. Does it blacken? Can you detect the odor of H_2S? Write the reaction.

THE KIPP'S APPARATUS.

To make hydrogen sulfid in large quantities we use the same method as in Exp. 81 a. But we make use of a device called the Kipp's apparatus named after its inventor. It consists of three larg

bulbs of glass, the two lower bulbs (b) and (e) being joined together while (a) having a long stem like a funnel is made to fit into (b) snugly and extends nearly to the bottom of (e) the lower bulb. The apparatus to be used must be charged as follows: First introduce a piece of glass wool or loose asbestos through the opening at (m), then through the same opening fill bulb (b) half full of large pieces of ferrous sulfid. The glass wool prevents small pieces of sulfid from falling into the lower bulb (e). Next close the opening (m) with a cork carrying a glass tube with a stop cock. In the top of the first bulb (a) place a cork containing a safety tube (t). Now through this tube pour a mixture of one part sulfuric acid to eight or ten of water, or hydrochloric acid (one to three) until the lower bulb is full and the acid covers a portion of the ferrous sulfid. Hydrogen sulfid is generated and escapes through the tube at (m). When you wish to stop the apparatus close this stop cock and the pressure of the gas forces the acid down into the bulb (e) and from there into bulb (a). The opening at (n) is intended for use in cleaning out the apparatus.



Such an apparatus should be used under a

hood as the hydrogen sulfid is very poisonous and should never be inhaled.

HYDROGEN SULFID AND METALS

Exp. 83. Pass gas from a Kipp's apparatus into test tubes containing solutions of (a) copper sulfate ($CuSO_4$), (b) mercuric chlorid ($HgCl_2$), (c) lead acetate, $Pb(C_2H_3O_2)_2$, (d) arsenic oxide(As_2O_3). Note colors in each case.

Reactions. $CuSO_4+H_2S=CuS$ (copper sulfid $+H_2SO_4$.

$HgCl_2+H_2S=HgS$ (mercuric sulfid) $+ 2\ HCl$.

$Pb(C_2H_3O_2)_2 + H_2S=PbS$ (lead sulfid) $+ 2\ HC_2H_3O_2$.

$As_2O_3 + 3\ H_2S = As_2S_3$ (arsenic sulfid) $+ 3\ H_2O$.

Exp. 84. Pass hydrogen sulfid into a solution of ferric chlorid ($FeCl_3$). It is reduced to ferrous chlorid and sulfur is precipitated.

Reaction. $2\ FeCl_3 + H_2S = 2\ HCl + 2\ FeCl_2$ (ferrous chlorid) $+ S$.

Note. Precipitation.

Many of the sulfids are insoluble in water, therefore when the gas is passed into solutions of certain metals these are thrown down or precipitated to the bottom of the test tube. A precipitate then is a solid formed from a substance that has been in solution.

HYDROGEN SULFID AND THE HALOGENS.

Exp. 85. Make a little chlorin water by heating a few crystals of potassium chlorate with concentrated hydrochloric acid. Into this solution run H_2S from a generator such as the Kipp's apparatus. Note the light yellow precipitate formed. Filter and burn the filter paper in the burner flame. Note the odor of the burning paper. What was the precipitate?

Try the same with bromin water, with a solution of iodin in water. In the last case filter out the precipitate then boil the liquid that runs through the paper until free from the odor of H_2S. This liquid which runs through is called the filtrate. Test this filtrate with a solution of lead nitrate, with mercuric chlorid, and note the color of the precipitates formed. See Exp. 70. What compound has the iodin formed with the H_2S?

Reactions.

a. $2KClO_3 + 4HCl = 2ClO_2 + 2H_2O + 2Cl + 2\,KCl$.

b. $H_2S + 2Cl = 2HCl + S$.

c. $H_2S + 2Br = 2HBr + S$.

COMPOUNDS OF SULFUR, HYDROGEN AND OXYGEN.

We have already learned that sulfur and oxygen combine to form two compounds, sulfur dioxid (SO_2) and sulfur trioxid (SO_3). These are the anhydrids of two acids, sulfurous (H_2SO_3) and sulfuric

acid (H_2SO_4). The former has but a limited use, chiefly for bleaching, but the other, sulfuric acid, is one of the most important compounds known to science. By means of sulfuric acid many other compounds are made There is hardly a trade or industry in which this acid is not used in some way or other.

There are many other acids of sulfur but none of any great importance as compared with the two named.

SULFURIC ACID.

Formula, H_2SO_4 Molecular weight, 98.

Sulfuric acid was known to the Arabian alchemist Geber as early as the 8th century. It was first described by Basil Valentine in the 15th century.

PREPARATION.

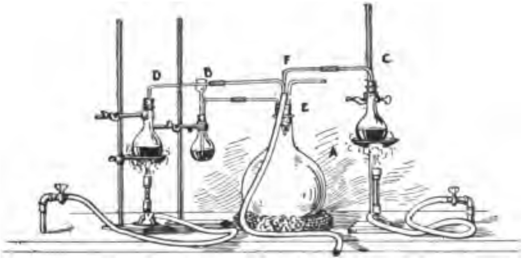
Exp. 86. To a small quantity of sulfur trioxid add a few drops of water. Note the hissing sound with which the two combine. Dilute the liquid thus made about ten volumes and then taste. Test with blue litmus paper. Examine a little commercial acid and test in the same way.

Sulfuric acid is made commercially by combining sulfur dioxid (SO_2), a gas called nitrogen dioxide (NO_2) and water in the form of steam. These are brought together in large chambers made

of lead.* The acid collects on the bottom of the chambers, is drawn off and concentrated.

The lead chamber process can be imitated on a small scale as follows.

Exp. 87. A large glass globe A is closed with a cork containing five glass tubes as shown in the figure. Four of these tubes reach nearly to the bottom of the globe, while one serves as an escape valve F. One of the tubes is connected with a flask D containing strong sulfuric acid and copper turnings for the generation of sulfur dioxid. Another, B, contains copper turnings and dilute nitric acid for the generation of nitric oxid and the last C contains water for the formation of steam.



The tube marked E is used to renew the supply of air from time to time during the process.

Begin the experiment by heating flask D. When this reaction begins pour dilute nitric acid

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*For a description of the lead chamber process see any complete chemical text. Very good descriptions are to be found in Roscoe and Schorlemmer's Treatise on Chemistry, and in Wagner's Chemical Technology.

into B (one part acid to three of water) and allow steam to enter the large bulb from C. It is well to have the water in C almost boiling when the nitric acid is placed in B. The main thing is to so time the reaction as to allow neither sulfur dioxid nor nitric oxid to escape into the room. The reactions which take place in the various parts of the apparatus are as follows:

D. $Cu + 2\ H_2SO_4 = CuSO_4$ (copper sulfate) $+ SO_2 + 2H_2O$.

B. $3\ Cu + 8\ HNO_3$ (nitric acid) $= 3\ Cu\ (NO_3)_2$ (copper nitrate) $+ 2\ NO$ (nitric oxid) $+ 4\ H_2O$.

A. $NO + O$ (oxygen from the air) $= NO_2$ (nitrogen dioxid sometimes called tetroxid).

A. $SO_2 + NO_2 = SO_3$ (sulfur trioxid) $+ NO$.

A. $SO_3 + H_2O = H_2SO_4$ (sulfuric acid).

The reaction is claimed by many chemists to be much more complex than here indicated, but the above is a general explanation of what takes place in the sulfuric acid factory. The supply of oxygen must be renewed in globe A whenever the red fumes of nitrogen dioxid can no longer be seen.

Exp. 88. After some acid has collected in the bottom of the receiver allow the apparatus to cool and test a small quantity with barium chlorid ($BaCl_2$). Note the precipitate. Try the same with dilute acid from your table. Are the two results the same?

Reaction. $BaCl_2 + H_2\ SO_4 = BaSO_4$ (barium

sulfate) + 2 HCl. The nitrogen dioxid serves as a carrier of oxygen from the air to the sulfur dioxid as the latter is not capable of taking up the oxygen directly.

The test with barium chlorid is the most common test for sulfuric acid.

The acid which you have made may be concentrated by evaporation in a porcelain dish over a water bath.

SULFURIC ACID AND WATER.

Sulfuric acid has so great an affinity for water that the two will combine with great evolution of heat. The acid can extract water from many substances in which it is combined.

Exp. 89. In about 50 c. c. of water in a beaker or evaporating dish place a thermometer. Now pour in about 10 c. c. of concentrated sulfuric acid. Does the temperature rise? 53

Exp. 90. To a small quantity of sugar in a test tube add a few drops of concentrated sulfuric acid. Note that the sugar blackens. Try the same with a bit of wood. These two substances are typical organic compounds and are composed of three constituents, carbon C, hydrogen and oxygen. Sugar, for example, has the formula $C_{12}H_{22}O_{11}$. Note that the hydrogen and oxygen are present in just the right proportions to form water. The sulfuric acid combines with these two elements and sets the carbon free.

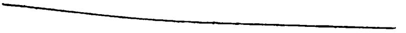
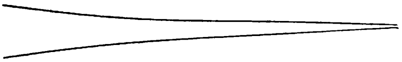
COMPARISON OF THE ELEMENTS OF THE OXYGEN FAMILY.

We have already noted that the three elements sulfur, selenium and tellurium have properties very similar to those of oxygen. These are chemical rather than physical properties as the latter differ widely. The four elements show about the same variation in physical properties that the Halogens do. The element of lowest atomic weight is a colorless gas, the next a solid, selenium is a heavier solid and tellurium a solid having marked metallic characteristics. The first element of the family is a strong non-metal and all the following elements are less non-metallic, i. e., partake more and more of the nature of a metal. In short, the physical properties of the elements vary with their atomic weights.

The chemical properties are very much alike. All form compounds with hydrogen in the ratio of one part of the element to two of hydrogen. Thus there are these compounds, water (H_2O), hydrogen sulfid (H_2S), hydrogen selenid (H_2Se) and hydrogen tellurid (H_2Te). These four compounds are analogous to the four formed with the halogens and hydrogen. They vary in stability with increasing molecular weight, i. e., H_2O is a very stable compound, H_2S less so, and the other two are so unstable that they can be made only with difficulty. The same variation is to be noticed in the four compounds, HF, HCl, HBr and HI.

All of these elements with the possible exception of tellurium exist in two allotropic forms. All except oxygen form compounds with oxygen which are acid anhydrids These acids are of little importance except in the case of sulfur so they will not be studied in detail. The study of this group is not completed so that the elements cannot be compared with respect to all their properties,

COMPARATIVE TABLE OF THE OXYGEN FAMILY.

	O	S	Se	Te
ATOMIC WEIGHT	16	32.06	79.1	125?
SPECIFIC GRAVITY OF SOLID..	..	2.04	4.5	6.25
MELTING POINT	..	114.	217.	500.
BOILING POINT	—181	440.	665.	above 1000.
APPEARANCE.	gas	yellow solid.	dark red powder.	silver white metallic appearance.
NON-METALLIC PROPERTIES ..				
MOLECULAR STRUCTURE.......	O_2	S_2	Se_2	Te_2
COMPOUNDS WITH HYDROGEN	H_2O	H_2S	H_2Se	H_2Te
STABILITY OF HYDROGEN COMPOUND				

THE NITROGEN FAMILY.

There are five elements which because of their similar chemical compounds are classed together. These are

NITROGEN..............	Symbol	N.	Atomic weight	14.03
PHOSPHORUS..		P		31.
ARSENIC....		As		75.
ANTIMONY..............		Sb(stibium)		120.
BISMUTH...		Bi		208.9

Notice that the difference in atomic weight is greater between antimony and bismuth than between any other two elements. It is believed that there is an unknown element that has an atomic weight between 120 and 208.9. This element would have properties varying between those of bismuth and antimony.

The last three elements in the above list are often classed with the metals and they will be again discussed under the subject of metals.

After the properties of the elements of this group have been discussed they can be compared as the elements of the other groups have been.

NITROGEN.

Symbol N. Atomic weight 14.03.

Discovered by Prof. Rutherford, of Edinborough, in 1772.

The name comes from the ancient name for saltpeter, and a Greek word meaning " to give rise to." Saltpeter is potassium nitrate, KNO_3.

Nitrogen occurs free in the atmosphere, of which it composes about 4-5, or 80 per cent., and in combination as nitrates, nitrites and ammonia.

The most simple method of preparation is from the air.

Exp. 91. Nitrogen from the air by means of phosphorous. In a slice of cork about half an inch thick and smaller than the mouth of a large bottle or jar, make a cavity and line with plaster of paris.

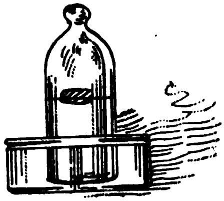
Make a paste by mixing the plaster with a little water. When the plaster is dry, place a dry piece of phosphorus about as large as a pea on the cork, float it on water in a basin filled with water, ignite the phosphorus with a hot wire and invert the bottle over it.

Reaction, 2 P (phosphorus) $+$ 5 O $= P_2O_5$ (phosphorus pentoxid).

$PO_5 + 3\ H_2O = 2\ H_3PO_4$ (phosphoric acid).

Note carefnlly the burning of the phosphorus. At last it will stop burning, although it may not all be consumed. Why? What is necessary in the air for combustion?

Note the white vapor. It is phosphorus pentoxid. It will be gradually absorbed and the gas in the bottle will become transparent, then you have nearly pure nitrogen left. Remove the bottle from the water, using a glass slip to cover it. Insert a burning splint. Does nitrogen burn or support combustion? What caused the phosphorus to burn? Why do we need any nitrogen in the air?



What is the proportion of the volume of nitrogen to the original volume of air?

Exp. 92. Taste the water from exp. 91. Test with blue and red litmus paper. What is its nature? See the equations under 91.

Exp. 93. Nitrogen from the air by means of cuprous chlorid Cu_2Cl_2.

Into a cylinder or long tube which is graduated into cubic centimeters pour a small quantity of fresh Cu_2Cl_2 solution. Read the volume of gas in the tube. Close with a stopper and shake. Allow to stand for three or four hours. Invert the tube in a basin of water. Note that the water rises in the tube to replace the oxygen which has been absorbed by the chlorid. Read the volume of gas in the tube. How does it compare with the original volume? Test the gas with a flame.

NITROGEN FROM A NITRITE.

Certain compounds of nitrogen give up nitrogen on being heated. Such a substance is ammonium nitrite (NH_4NO_2). This reaction is too violent for common use. A better way is to mix ammonium chlorid and sodium nitrite ($NaNO_2$).

Exp. 94. Fit a small flask with a cork and delivery tube. In it place a mixture of about 10 grams of NH_4Cl with 15 g. $NaNO_2$. Fill the flask one-quarter full of water and heat. Nitrogen will be set free and may be collected over water. When the evolution of gas has begun the lamp may be removed and the gas will continue to be set free without further heating. Test the nitrogen thus made with a flame.

Reactions.

NH_4NO_2 (ammonium nitrite) heated =
$2H_2O + 2N$.
NH_4Cl (ammonium chlorid) + $NaNO_2$ (sodium nitrite) = $2N + NaCl$ (sodium chlorid) + $2H_2O$.

Nitrogen may be made from its compounds in many other ways but the methods are all unimportant.

THE ATMOSPHERE.

A mixture of oxygen and nitrogen.
Specific gravity 1.
Specific density or weight as compared with a like volume of hydrogen 14.39.

In the early days of science the name air was applied to any gaseous body. To-day the term has a restricted application meaning simply the gaseous sphere that surrounds the earth and from which we take the oxygen we breathe. The gaseous sphere is also called the atmosphere.

We know that we are surrounded by a gaseous medium because we can feel it in motion when the wind blows, it offers resistance to bodies passing through it, and we can determine its weight and pressure. For example, if a glass globe is weighed before and after exhausting the air from it the weight of the air which it contained may be determined. It has been shown by many careful determinations that the weight of one liter of air under

normal conditions of pressure and temperature is 1.2935 grams.

The pressure of the atmosphere is about 15 pounds (14.73) to the square inch or 1033.3 grams to the square centimeter. It is measured by an instrument called the barometer. This is a long glass tube closed at one end and filled with mercury and inverted in a dish containing mercury. It was noticed that when the tube is inverted the mercury will not run out but will fall to a level of about 30 inches above the level of the mercury in the dish and will remain there. The weight of the air is such as to just counterbalance a column of mercury of known diameter and about 30 inches in length and is just equal to the weight of a column of air of equal diameter and a length as great as the height of the atmosphere.

The height to which the atmosphere extends is not exactly known. Its extent is believed to be about 50 miles.

The atmosphere is not a chemical compound, but a mixture of several gases. The two chief constituents are oxygen and nitrogen. These compose about 99.75 per cent. of the air, while the remaining 25 per cent. consists of ammonia, water vapor, carbon dioxid, compounds of sulfur such as H_2S and SO_2, hydrogen dioxid, oxids of nitrogen, and the newly discovered elements Argon, Neon, Krypton and Xenon.

The quantities of most of these lesser constituents vary with the locality. For example the air will contain a large amount of impurity in a city while the quantity will be very small in the country. The water vapor varies with the temperature. If a cubic meter of air is saturated with water vapor at 0 degrees it will hold 4.8 grams of water, and at 35 degrees, which is about the highest summer temperature in this latitude, it will hold 39.2 grams. This atmospheric water is precipitated when the atmosphere is cooled. If the change is small the water will appear as dew, if sudden, as rain or snow. The quantity of water which the atmosphere will hold is greatest in tropical climates hence the annual rain fall is greatest toward the equator and falls off toward the poles.

Carbon dioxid comes into the air from many sources, such as the decomposition of vegetable matter and the combustion of fuel. The sulfur compounds come both from the decomposition of vegetable and animal matter and from the burning of coal.

The two chief constituents of the air are present in the proportions of about four parts of nitrogen to one part of oxygen. Nitrogen is a very inactive gas, combining with all other elements only with the greatest difficulty. It serves to dilute the oxygen and adapt it for purposes of breathing and combustion.

We know that air is a mixture and not a chemical compound, for several reasons. 1. The two gases, nitrogen and oxygen, may be mixed in the proportion in which they occur in the air, and no change in temperature will take place. Now, whenever a chemical compound is made heat is either absorbed or evolved.

2. The two constituents show a slight variation in their proportions which is never the case in a true chemical compound.

3. When air is dissolved in water more oxygen dissolves than nitrogen, which could not be the case were the air a compound. Many other considerations show that air is a mixture.

Air may be reduced to a light blue liquid by great pressure and cold. Liquid air is now a regular article of commerce. The chief value of liquid air is its power to produce great cold.

NITROGEN AND HYDROGEN.

Nitrogen forms three compounds with hydrogen, of which one, ammonia (NH_3), is by far the most important. The others are hydrazin (N_2H_4) and azoamid (N_3H). The latter are better known in their organic compounds, and are usually studied under organic chemistry.

AMMONIA.

Formula, NH_3. Molecular weight 17.03

Ammonia, in the form of its compounds, has

been known since the time of the early alchemists. Its compounds were imported into Europe at a very early date, from the far East, quantities being found in the Libyan desert, near the temple of Jupiter Ammon, whence the name ammonia. The gas itself was not recognized as a distinct compound until made by Priestly in 1774.

Preparation.

Exp. 95. Ammonia from ammonium chlorid, (NH_4Cl) and calcium hydroxid ($Ca(OH)_2$).

Pulverize about a gram of ammonium chlorid and note its odor. Note the odor, if any, of calcium hydroxid. Mix the chlorid and the hydroxid and note the odor again. Is there any difference? Remove the mixture to a dry test tube and heat high above the Bunsen flame.

Reaction. $2NH_4Cl$ (ammonium chlorid) + $Ca(OH)_2$ (calcium hydroxid) = $CaCl_2$ (calcium chloid) + $2NH_3$ (ammonia) + $2H_2O$.

In this reaction the water will condense on the upper part of the test tube and is liable to run down the tube striking the warmer parts thus breaking it. If the tube is kept warm along its entire length this will not occur.

The reaction works about as well with unslaked lime (CaO). In the latter case less water is formed. Write the equation.

Exp. 96. Bring a rod moistened with HCl to the mouth of a tube generating ammonia. What is

formed. Write the reaction. See hydrochloric acid Exp. 46.

Insert a piece of moist red litmus paper in the tube. How does this reaction differ from a similar one under hydrochloric acid?

Exp. 97. Pulverize about two grams of ammonium chlorid in a mortar and mix well with about twice as much calcium hydroxid. Place the mixture in a tube or small flask to which a delivery tube has been attached. Attach the delivery tube to a tube filled with small pieces of lime. This will dry the ammonia gas.

Collect several jars of the gas by upward displacement of mercury.

Exp. 98. Prepare a bottle or small jar with a jet tube, as in Exp. 46, and perform the same experiment using ammonia instead of hydrochloric acid and a red litmus solution instead of a blue. Is ammonia very soluble in water? What is the ordinary commercial ammonia?

Exp. 99. Insert a burning splint in a bottle of ammonia gas. Does the gas burn or support combustion? Note the odor of ammonia.

Exp. 100. To show the combustion of ammonia.

Ammonia does not burn well under ordinary circumstances. Under a hood heat a small beaker containing concentrated ammonia solution. From a gas holder run a rapid stream of oxygen through

the liquid. Now lower a glowing platinum wire into the beaker. What happens?

Exp. 101. Make a solution of ammonia in water by passing the gas into cold water. Carefully taste a drop of the solution thus made. Note the action on litmus. Is it the same as that of the gaseous ammonia? To a small quantity of the solution add a little litmus solution then drop by drop dilute hydrochloric acid until the color of the litmus changes. When this occurs the ammonia has been all neutralized by the acid. Evaporate the solution to dryness and examine the residue. Carefully taste. Dissolve a little in water and test for chlorin. Treat another portion with potassium hydroxid, warm and note the odor of the escaping gas. What is it? Heat a small quantity of the residue on platinum foil. What does it do? From all these tests can you tell what the residue is? Write all the reactions involved in this experiment.

Exp. 102. Treat another small quantity of the ammonia solution you have made, or what will do just as well, the commercial ammonia, with a solution of ferric chlorid $FeCl_3$, another portion with copper sulfate $CuSO_4$, and a third with Nessler's reagent.**

**NESSLER'S REAGENT.

Nessler's reagent is a mixture of the double iodid of potassium and mercury ($HgI_2 2KI$) and potassium hydroxid. It is made by dissolving 3.5 grams of KI in 100 c. c. water, then dissolving 1. 6 g. $HgCl_2$ in 30 c.c. of water. Add mercury solution gradually to the iodid solution, stirring constantly, until the precipitate first formed no longer dissolves.

REACTIONS FOR AMMONIA.

1. NH_4OH (ammonia) + $FeCl_3$ (Ferric chlorid) = $Fe(OH)_3$ (Ferric hydroxid)+$3NH_4Cl$.

2. Any copper salt with ammonia will form at first a light blue precipitate then a deep blue solution.

$4NH_4OH + CuSO_4 = CuSO_4 (NH_3)_4 H_2O + 3H_2O$.

3. $4NH_4OH + 2HgI_2\ 2KI + Hg_2\ I(NH_2)\ O + 4KI + 3NH_4I + 3H_2O$.

Ammonia is made in nature by the decomposition of certain organic compounds which contain nitrogen.

Exp. 103. Mix a small quantity of slaked lime, i. e. calcium hydroxid, with dry sodium hydroxid. Cut a small piece of flannel into little pieces and heat with the above mixture. Note that the escaping gas is ammonia.

NITROGEN AND THE HALOGENS.

Nitrogen forms compounds with the halogens which are so very explosive that they are not at all adapted for laboratory experiments.

The two most important halogen compounds are nitrogen trichlorid—(NCl_3) and nitrogen triiodid (NI_3,) the former being about the most dangerous explosive known.

NITROGEN AND OXYGEN.

There are five compounds of nitrogen and oxy-

gen. Three of these are the anhydrids of acids, as follows:

1. N_2O = nitrous oxid. The anhydrid of hyponitrous acid (HNO).

2. NO = nitric oxid.

3. N_2O_3 = nitrogen trioxid. Anhydrid of nitrous acid (HNO_2).

4. NO_2 = nitrogen dioxid or nitrogen peroxid.

5. N_2O_5 = nitrogen pentoxid. Anhydrid of nitric acid (HNO_3).

Three of these oxids are gases, nitrous, nitric and nitrogen dioxid. Nitrogen trioxid exists as a liquid, of a blue color, which boils at a very low temperature, decomposing into nitrogen dioxid and nitric acid. Nitrogen pentoxid, the anhydrid of nitric acid, is a crystalline solid. It decomposes readily into nitrogen dioxid and oxygen as follows:

$$N_2O_5 = 2NO + O,$$

Only the gaseous oxids may be studied in an elementary course.

NITROUS OXID.

Formula N_2O. Molecular weight 44.

Discovered by Priestley in 1772.

The gas is also called laughing gas because of the peculiar intoxication which it produces when inhaled. It produces insensibility to pain and is much used in minor surgical operations, such as in dentistry, etc.

Preparation. Nitrous oxid is usually made in small quantities by heating ammonium nitrate NH_4NO_3.

NH_4NO_3 heated $= N_2O + 2H_2O$.

The evolution of gas is so rapid that an explosion often occurs. The gas may be prepared without danger, as follows:

Exp. 104. Grind together 2 grams of ammonium sulfate $(NH_4)_2SO_4$ and 3 grams of sodium nitrate $NaNO_3$. Place in a small flask or test tube arranged with a delivery tube and heat gently. Collect the gas over hot water. Collect one jar by downward displacement.

Reaction.

$(NH_4)_2SO_4 + 2NaNO_3 = 2N_2O + Na_2SO_4$ sodium sulfate $+ 4H_2O$.

Exp. Note the odor of the gas. Test the contents of one jar with a burning splint. Into another which has a small quantity of hot water in the bottom lower a deflagrating spoon containing a piece of phosphorous no larger than a grain of wheat. Ignite the phosphorous with a hot wire.

Exp. 106. Ignite a quantity of sulfur in a deflagrating spoon and immediately lower into a jar of the gas. It will be extinguished. Remove and allow to burn violently in the air then repeat the experiment. It will now burn in the gas.

Exp. 107. Mix equal quantities of nitrous oxid and hydrogen and apply a flame. What other gas does nitrous oxid most resemble?

NITRIC OXID.

Formula NO. Molecular weight 30.

First observed by Van Helmont, and was later investigated by Priestly, the discoverer of nitrous oxid.

Preparation.

Nitrous oxid is made when nitric acid dissolves metals.

Exp. 108. Place a few pieces of metallic copper in a flask fitted with a delivery tube and on them pour a mixture of equal volumes of concentrated nitric acid and water. Use just enough acid to cover the copper. If the action does not start at once warm the flask a little. Collect the gas over water. Collect four jars of the gas.

Do not allow the nitric oxid to escape into the room as the fumes are very disagreeable. Perform all the experiments under a hood.

Exp. 109. Pass the gas into a solution of ferrous sulphate ($FeSO_4$). Note the brown color. Heat the solution. What happens?

Exp. 110. Test a jar of the gas with a burning splint. Admit air to another jar and note the brown fumes. These are fumes of nitrogen dioxid (NO_2).

$$NO+O=NO_2.$$

Exp. 111. Into a jar of the gas pour a few drops of carbon disulfid (CS_2). Cover with a glass plate and shake. Apply a flame to the mouth of

the jar. This shows that nitric oxid supports combustion although not as well as nitrous oxid.

The same fact may be shown by lowering a piece of phosphorous into a jar of the gas immediately after the phosphorous has been lighted. It will be extinguished but if allowed to become well inflamed and then lowered into the gas it will continue to burn.

Exp. 112. Evaporate the solution remaining in the generating flask to dryness. You have a salt. What is it?

Reactions.

The reactions for the formation of nitric oxid are very complicated. For a complete understanding of them it is necessary to understand several facts, i. e. 1. Nitric acid if concentrated will oxidize nitric oxid to nitrogen dioxid, and to nitrogen trioxid. 2. Nitrogen dioxid with water is changed to nitric acid and nitric oxid.

In the first reaction between the nitric acid and the copper the latter is oxidized to copper oxid CuO, two molecules of the acid giving up one atom of oxygen i. e.

1. $2HNO_3=2NO_2+H_2O+O$.
2. $Cu+O=CuO$.

Combining 1 and 2 we have

3. $2HNO_3+Cu=CuO+2NO_2+H_2O$.

But copper oxid is a base and with nitric acid it will form a salt, i.e. copper nitrate. $Cu(NO_3)_2$.

4. $CuO+2HNO_3=Cu(NO_3)_2+H_2O$.

The reaction showing the formation of nitrogen dioxid would be

5. $Cu+4HNO_3=Cu(NO_3)_2+2H_2O+2NO_2$.

But nitrogen dioxid and water combine to form nitric acid and nitric oxid.

6. $H_2O+3NO_2=2HNO_3+NO$.

Or the full reaction reduced to lowest terms is

7. $3Cu+8HNO_3=3Cu(NO_3)_2+2NO+4H_2O$.

NITROGEN DIOXID.

Formula, NO_2. Molecular Weight, 46.

Also called nitrogen peroxid.

Preparation.

This gas may be made in many ways. The most simple method is one we have already seen, admit air to a jar of nitric oxid. It has been prepared by heating a nitrate of a metal having a high specific gravity, as for example $Pb(NO_3)_2$.

In a test tube of hard glass arranged with a delivery tube heat 10 grams of lead nitrate. Collect the gas given off by downward displacement. Test a jar of the gas with burning phosphorous. Observe all the precautions concerning phosphorous. How does the gas support combustion as compared with the other oxids we have studied?

Exp. 114. In a jar of the gas pour a few drops of water. Cover with a glass plate and shake until the brown color of the gas disappears. Test

the liquid with litmus paper. Carefully taste a drop. What kind of a liquid is it?

Exp. 115. Pour a few drops of a solution of potassium iodid into a jar of the gas. Note the effect. This is a common test for nitric oxid.

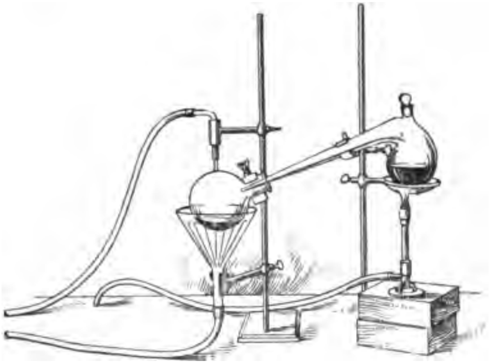
ACIDS OF NITROGEN.

There are three, hyponitrous (HNO), nitrous (HNO_2) and nitric (HNO_3). Of these the first two are of comparatively little importance.

NITRIC ACID.

Formula, HNO_3. Molecular Weight, 63.

Nitric acid was first prepared by the Alchemist Geber in the 9th century. He made it by heating together potassium nitrate (KNO_3) and ferrous sulfate ($FeSO_4$).



Preparation.

Exp. 116. Arrange a glass stoppered retort

so that it may be heated. Place the outlet tube called the retort neck in a flask immersed in running water. The best arrangement for running water is to place the flask in a large funnel and allow water to flow onto it from a tap above. Attach a rubber tube to the funnel stem to carry off the waste.

In the flask place about 30 grams of sodium nitrate ($NaNO_3$), also called Chili Saltpeter. Carefully pour on the salt 10 c. c. of concentrated sulfuric acid. Be careful not to let the acid fall into the neck of the retort. Replace the glass stopper and heat gently until no more liquid passes into the condensing flask. Be careful not to heat too rapidly or the flask contents will foam violently.

Properties of nitric acid.

Exp. 117. Note the odor and the color of the acid. Hold a glass rod dipped in ammonia over the mouth of the receiving flask. Note the white fumes. What are they? Dilute a small quantity of the acid you have made with about 20 volumes of water and very carefully taste a drop. Test with litmus paper.

Nitric acid as an oxidizing agent.

We have already seen that an oxidizing agent is a substance which will give up its oxygen readily to other substances. Nitric acid and its salts are typical oxidizing agents as they will all give up their oxygen readily.

Exp. 118. Pulverize a small quantity of charcoal and heat it in an iron spoon or in a porcelain crucible. When hot pour a small quantity of the freshly made nitric acid upon it. The charcoal will burn and during the combustion copious red fumes will be given off. What are they?

Reaction,

C (carbon) $+2HNO_3{=}{=}H_2O+CO_2$ (carbon dioxid)$+2NO_2$.

The carbon has been oxidized and the nitric acid reduced.

Exp. 119. Pour a few c. c. of concentrated nitric acid over a small amount of fine sulfur in a test tube and heat. Note that the sulphur disappears. Dilute with water and after filtering, test the clear filtrate with a solution of barium chlorid ($BaCl_2$). What has been formed? Write the reaction.

Exp. 120. Dip a piece of woolen cloth into dilute nitric acid. After standing a little time wash and note the yellow color of the cloth. All organic compounds such as wool, hair, the skin, etc. which contain nitrogen are colored yellow by nitric acid.

Exp. 121. Nitric acid and metals.

Treat the following metals with dilute nitric acid. Copper, (Cu), Iron (Fe), Lead (Pb), Magnesium (Mg), and Tin (Sn). Note the gas formed in each case. Write the reactions.

Treat a small piece of gold with the acid. Gold leaf is best. Note the effect. Try another piece with hydrochloric acid. Mix the two acids and try again. Does the gold dissolve? This mixture of nitric and hydrochloric acids is called aqua regia or nitro-hydrochloric acid.

Nitric acid is often used to etch metals. Cover a piece of brass or other metal with paraffin. Write on the paraffin with some sharp instrument, being careful to scratch through the coating. Along the lines of the writing pour a few drops of nitric acid and allow to stand. Clean off the paraffin and note that the writing has been etched on the metal.

Exp. 122. Qualitative tests for nitric acid and nitrates.

A qualitative test is one which merely shows the presence of a substance. A quantitative test on the other hand is one which shows the presence and at the same time the amount of a substance.

In a small quantity of indigo solution pour a few drops of nitric acid. The blue color of the solution will disappear.

Into dilute nitric acid drop a crystal of ferrous sulfate ($FeSO_4$). Note the brown color about the crystal.

Exp. 123. The brown ring test for nitric acid.

Dissolve a little KNO_3 or $NaNO_3$ in water. Add a little ferrous sulfate solution. Incline the test tube and allow strong H_2SO_4 to run down the

side. Note the effect where the acid and other liquids meet. This is the most common test for nitric acid and the nitrates.

Reaction. The brown ring test may be represented in an equation thus: 2 KNO_3 + 4 H_2SO_4 + 10 $FeSO_4$=K_2SO_4 (potassium sulfate) + 3 $Fe_2(SO_4)_3$ (ferric sulfate) + 4 H_2O + 2 $(FeSO_4)_2NO$.

The last compound has no specific name and its composition is involved in uncertainty. (Prescott & Johnson).

Exp. 124. Composition of nitric acid.

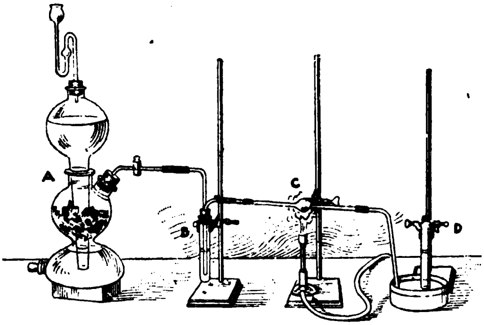
In a small flask or bottle arranged with a stopper carrying a delivery tube and funnel tube, place a few pieces of magnesium ribbon. Pour onto the ribbon a small quantity of dilute nitric acid. Collect the gas which escapes and test with a flame. The gas is hydrogen. As it could not have come from the magnesium or from the water it must be from the nitric acid. Hence one constituent of nitric acid is hydrogen.

Exp. 125. Arrange a Kipps apparatus for the generation of carbon dioxid (CO_2) by placing pieces of marble ($CaCO_3$) in the middle part of the apparatus and dilute hydrochloric acid in the upper. On opening the stop cock the acid will come in contact with the marble and carbon dioxid will be generated.

Reaction.

$CaCO_3$ + 2HCl = $CaCl_2$ (calcium chlorid) + CO_2+H_2O.

Fit a large test tube with a stopper having two holes, one containing a long glass tube which reaches to the bottom of the test tube and the other a short tube bent at right angles. Cover the bottom of the test tube with concentrated nitric acid and connect the longer tube with the carbon dioxid generator by means of a rubber tube, and the other with a bulb tube of hard glass, arranged



as as in the figure. The end of the bulb tube is fitted with a glass delivery tube which dips under the mouth of a test tube filled with concentrated sodium hydroxid solution and immersed in a beaker filled with the same.

In the bulb tube place a few pieces of clean copper filings. Arrange to heat.

In the figure, A is the Kipps apparatus, B is the test tube with concentrated nitric acid, C the bulb tube containing the copper and D the test tube

immersed in sodium hydroxid solution.

Now allow a slow stream of carbon dioxid to flow through the apparatus to drive out all the air. While doing this remove the delivery tube leading from C to D from the mouth of the test tube. After the air is all driven out heat the acid in B and the copper in C. Collect the gas which is given off in the test tube at D. The carbon dioxid will drive the nitric acid over the hot copper and the acid will be decomposed into its constituents.

When D is nearly full, stop the heating and disconnect the apparatus while still hot. Allow the gas in D to stand a few minutes and then test with a burning splint. Recognize the gas as nitrogen. The sodium hydroxid solution will absorb all the carbon dioxid.

Examine the contents of the bulb tube. The copper has been turned black. This is due to the formation of copper oxid (CuO). The oxygen must have come from the nitric acid as it can be proved that the carbon dioxid does not give up its oxygen under these circumstances. Hence we have proven that nitric acid contains the three elements hydrogen, oxygen and nitrogen. Other considerations show that these are present in the proportion of one atom of hydrogen to one of nitrogen to three of oxygen.

Reactions for the formation of nitric acid.

We made the acid from sodium nitrate and

It is a white wax-like solid, very poisonous and extremely inflammable. Under certain conditions it crystallizes in octahedral prisms.

Red phosphorous is made from the white by heating the latter in the absence of air to about 300 degrees Centigrade. It is a non-crystalline solid, when pure having no taste or odor, is of a deep red color, is non-poisonous and takes fire only when heated to about 260°. In every respect it is so totally different from the white variety as to seem to be a different element. If it is heated to about 360° in the absence of air it will turn back to the white variety.

The third form is made when red phosphorous is heated to 580° under great pressure. It is a dark red metallic substance crystallizing in rhombohedral forms.

Exp. 126. Examine a piece of white phosphorous. Note the color, odor, etc. Always handle this element with tongs, never with the fingers. Keep the piece which you are examining wet to prevent its taking fire. Remember that phosphorous takes fire at a very low temperature and that a burn is very painful and slow to heal.

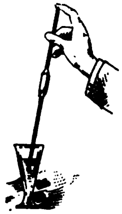
Dry a piece of phosphorous as large as an apple seed very carefully on blotting paper, place on a small board and rub gently with another board. The friction will ignite the element. Touch another small piece with a test tube con-

taining warm water. The phosphorous will inflame.

In performing these experiments the element must be dry otherwise it will explode on ignition and burning phosphorous will be scattered about.

Exp. 127. Heat a small quantity of lampblack in an iron spoon or crucible. Allow to cool then pour it over a little piece of phosphorous. The lampblack is a very porous substance which can absorb large quantities of gases. On being heated in the air it will absorb much oxygen and this is present in sufficient quantity to ignite the phosphorous.

Exp. 128. Place a piece of phosphorous about as large as an apple seed in a six-inch test tube and fill one-half full of water. Drop in three or four large crystals of potassium chlorate ($KClO_3$). Insert a thistle tube, placing thelower end near or on the phosphorous, then pour two or three c. c. of H_2SO_4 through the tube. Note the effect.



Phosphorous has so great an affinity for oxygen that it will combine with it with evolution of heat and light even under water.

Reaction. The potassium chlorate combines with the sulfuric acid to form chloric acid ($HClO_3$), a substance which is very easily decomposed giving off chlorin and oxygen.

$2KClO_3 + H_2SO_4 = K_2SO_4$ (potassium sulfate) + $2HClO_3$.

$2HClO_3 = HClO_4$ (chloric acid) + $H_2O + ClO_2$ (chlorin dioxid).

The chlorin dioxid in turn breaks up into chlorin and oxygen.

Exp. 129. Examine red phosphorous. Try to ignite it. Compare with the white variety.

PROBLEMS.

1. If 5 g. of phosphorous is allowed to burn completely in a quantity of air, how much air would be necessary and how much nitrogen would be left?

2. How much nitric acid may be obtained from 500 g. $NaNO_3$? How many c. c. of sulfuric acid would be required to set the nitric acid free if the sulfuric acid has a specific gravity of 1.79?

3. How many grams of $Cu(NO_3)_2$ would be formed from 130 c. c. HNO_3 having a specific gravity of 1.17?

PHOSPHOROUS AND HYDROGEN.

There are several compounds of phosphorous and hydrogen only one of which is of much importance. This is the compound analogous to ammonia, Phosphin, PH_3.

Phosphin is made when white phosphorous is boiled with a concentrated solution of sodium hy-

droxid. It is a gas of very disagreeable odor, is poisonous and ignites spontaneously in the air. (Due to the presence of P_2H_4). It forms a class of compounds analogous to those formed by ammonium and these are called phosphonium compounds.

Phosphin should be made by the teacher as it is too dangerous for students to experiment with.

PHOSPHOROUS AND THE HALOGENS.

Phosphorous, like nitrogen, forms compounds with the common halogens. These are not explosive as are the nitrogen compounds but have very disagreeable odors and are difficult to work with.

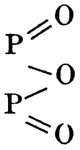
Exp. 130. On a small dry piece of white phosphorous place a crystal of iodin. The two elements will combine with a flame. Examine the residue. This is phosphorous triiodid PI_3.

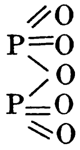
Phosphorous forms two classes of compounds with the halogens and in some cases more than two. In one class the phosphorous occurs as an element having a valence of three and in the other having a valence of five. Thus we have PCl_3 and PCl_5, PBr_3, PBr_5, PI_3, PI_5, etc. All of these compounds except PI_3 are too difficult for the beginner to make.

PHOSPHOROUS AND OXYGEN.

There are two compounds of oxygen and phosphorous in which phosphorous acts as a tri and

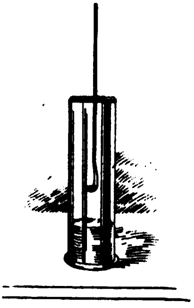
penta-valent element. Thus we have P_2O_3 and P_2O_5, or arranged so as to show the valence





The trioxid is somewhat difficult to make but the pentoxid is formed whenever phosphorous is burned in the air. The trioxid is made by burning phosphorous with an insufficient amount of air. It is a white powder with an odor like that of garlic. It will burn and by its combustion forms P_2O_5.

Exp. 131. Phosphorous pentoxid made by burning phosphorous in air.



Fit a wide-mouthed bottle with a close fitting cork or rubber stopper. In the stopper fasten an iron deflagating spoon as in the figure. In the spoon place a piece of phosphorous and lower into the bottle closing it tightly. The bottle and phosphorous must be dry. Ignite the phosphorous by means of a strong burning lens such as that in an ordinary reading glass. If sunlight fails, ignite by means of a hot wire before the bottle is closed. Note the white powder forming on the sides of the bottle. When the phosphorous stops burning open the

mouth of the bottle under water. Does the water rise?

Exp. 132. Repeat the above experiment using pure oxygen instead of air. In the resulting product the same? Do not open the bottle under water this time. When the combustion has ceased pour a few drops of water into the bottle and shake. Does the phosphorous pentoxid dissolve? Test the solution with blue litmus paper. Taste a drop from a glass rod.

Phosphoric acid has been formed according to the following reaction.

$$3H_2O + P_2O_5 = 2H_3PO_4.$$

Likewise when the phosphorous trioxid is dissolved in water an acid is formed having the formula H_3PO_3. This is called phosphorous acid.

There are several other acids of phosphorous but those named are the most important. Besides phosphoric and phosphorous acids we have the following.

H_3PO_2.	Hypophosphorous acid.
$H_4P_2O_6$.	Hypophosphoric acid.
$H_4P_2O_7$.	Pyrophosphoric acid.
HPO_3.	Meta phosphoric acid.

Read again the article on the naming of acids and their salts.

Phosphoric acid is sometimes called orthophosphoric acid. The term "ortho" means right or correct and is applied to those acids which have

the greatest number of OH groups possible for the valence of the principal element. In H_3PO_4 we have the greatest number of OH groups possible for the valence of phosphorous which is 5.

The term "pyro" means fire and denotes that the compound has been formed by means of heat, i. e., pyrophosphoric acid is made from ortho by means of heat.

Meta means "after" and in the case of acids denotes that the compound has been formed from the corresponding ortho acid by the withdrawal of water. In this case metaphosphoric acid is formed from ortho by the withdrawal of one molecule of water.

$$H_3PO_4-H_2O==HPO_3.$$

ARSENIC.

Symbol, As. Atomic Weight, 74.0.

Known from the earliest times. First mentioned by Aristotle. White arsenic (As_2O_3) was first spoken of by the alchemist Geber in the 8th century. Arsenic was much used by the alchemists as by its aid copper could be turned to a white color and this was believed to be a change from copper to silver.

Arsenic is better known in its compounds than in the free state. The most common compound is arsenic trioxid or white arsenic As_2O_3.

Exp. 133. Heat a small piece of metallic ar-

senic in a small tube of hard glass, closed at one end. What forms in the tube?

Dissolve a small piece of arsenic in concentrated nitric acid. What is formed?

ARSENIC AND OXYGEN.

There are two compounds of arsenic and oxygen, arsenious oxid (As_4O_6) or as commonly written (As_2O_3) and arsenic pentoxid (As_2O_5). The former is quite common while the latter is comparatively rare.

Exp. 134. Preparation of As_2O_3.

Heat a small quantity of powdered arsenic in a hard glass tube closed at one end. Examine the compound thus formed with a lens.

Mix a small quantity of As_2O_3 with a little powdered charcoal and heat in a glass tube. Note the effect of the charcoal on the oxid. What is reduction? What is oxidation?

Exp. 135. Dissolve a little As_2O_3 in warm concentrated hydrochloric acid. Dilute with an equal amount of water.

Into one portion of this solution run H_2S. Note the precipitate. What is it? Write the reaction.

Filter the precipitate and on the filter paper pour a few drops of hot yellow ammonium sulfid $(NH_4)_2Sx$. The arsenic precipitate dissolves forming an ammonium thioarsenate.

Reaction.

$As_2S_3 + 4(NH_4)_2Sx = 2\ (NH_4)_4\ AsS_3 + S.$

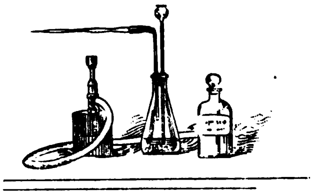
The x in the $(NH_4)_2Sx$ indicates that the quantity of sulfur is unknown. In writing the reaction we have assumed that x=2.

Reinsch test for arsenic.

In another portion of the arsenic solution made above hang a clean bright piece of copper wire or foil. The arsenic will be deposited upon it. Place the wire in a small tube of hard glass and heat. The metallic arsenic will sublime to a cooler part of the tube and be deposited there as a bright mirror. This is one of the most delicate tests for arsenic.

Exp. 136. This should be performed by the teacher as the compound of arsenic arsin (AsH_3) is very poisonous.

Arrange a small hydrogen generator. To the outlet tube attach a bulb tube filled with granulated calcium chlorid ($CaCl_2$). To the bulb tube attach a straight tube of hard glass having two constrictions as shown in the figure. The end of the tube should be drawn out to a fine point. In the generator place a little zinc, wrap the generator in a cloth which in case of an explosion will stop splinters of glass. Pour dilute sulfuric acid onto the zinc and when the hydrogen is generating free-



ly pour into the flask a few c. c. of arsenic solution. Test the gas to see if it is free from air and when this is the case light it at the jet. Note the color of the flame. In the flame hold a piece of cold porcelain. Note the arsenic spots formed. Test the same with a drop of sodium hypochlorite solution ($NaOCl$). The spot dissolves. Try the same with hot nitric acid. Place a burner under the outlet tube. Note the deposit of arsenic on the cold part of the tube.

Reaction. The arsenic unites with the hydrogen formed by the action of the zinc and the acid forming arsin (AsH_3). This burns in the air genrating As_2O_3 and water. If a cold object is held in the flame metallic arsenic is deposited upon it. Likewise if the gas is heated it is decomposed and metallic arsenic is deposited.

Arsenic compounds are very poisonous and it is often the duty of the chemist to detect them in suspected cases of poisoning. For this purpose the two tests of Reinsch and Marsh are used.

The antidote for arsenic is freshly precipitated ferric hydroxid $Fe(OH)_3$ which forms a compound which is insoluble.

ACIDS OF ARSENIC.

There are two acids of arsenic corresponding to the two anhydrids As_2O_3 and As_2O_5. These are arsenious acid and arsenic acid H_3AsO_3 and H_3AsO_4.

ANTIMONY.

Symbol, Sb. Atomic Weight, 119.52.

The symbol comes from the Latin name for antimony (Stibium).

Antimony belongs to the same family of elements as phosphorous and arsenic but it is so metallic in its properties that it is usually considered among the metals.

Exp. 137. Repeat the Marsh experiment using a solution of antimony. Compare the antimony mirror with the arsenic. Compare the spots on porcelain. Test the antimony spot with fresh sodium hypochlorite solution. Test spot with nitric acid. Spot turns white. Test with a crystal of iodin.

Reaction. The reaction is the same as in the case of the arsenic except that a compound of antimony and hydrogen is formed called stibin (SbH_3).

Exp. 138. In each of three test tubes place a small piece of antimony. In one pour a little concentrated hydrochloric acid, in another nitric and in the third a mixture of the two acids. The mixture is called nitrohydrochloric acid or aqua regia.

Heat the contents of each tube and note the result. To a small portion of the nitrohydrochloric acid solution thus made add a little water. A white precipitate is formed. This is SbOCl (antimony oxychlorid). Write the reaction.

Test another portion with H_2S. Sb_2S_3 is form-

ed. Treat the Sb_2S_3 with warm ammonium sulfid. A solution is formed from which the antimony may again be precipitated by means of hydrochloric acid.

Test a third portion with sodium hydroxid. Does the precipitate dissolve in excess of the reagent?

Reaction.

a. $SbCl_3+3NaOH=SbOOH+3NaCl+H_2O$.

b. $SbOOH+NaOH=NaSbO_2+H_2O$.

PROBLEMS.

1. What weight of phosphorous can be obtained from 260 grams of bone ash if the ash contains 60 %. $Ca_3(PO_4)_2$?

2. How much phosphorous pentoxid can be made from the amount of phosphorous obtained above? To how much phosphoric acid would the pentoxid correspond?

3. How much arsin (AsH_3) can be made from 2.5 grams of arsenic trioxid? How much zinc would be needed if zinc were used?

4. If 10 g. antimony are treated with Cl to form $SbCl_3$, how much HCl would be necessary to give the proper amount of Cl? How many liters of H_2S must be run into the $SbCl_3$ to change it to Sb_2S_3 if H_2S weighs 17 times as much as hydrogen?

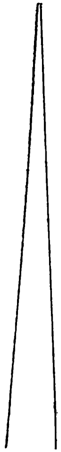
COMPARISON OF ARSENIC AND ANTIMONY REACTIONS.

REACTIONS OF THE METALLIC SPOTS FORMED FROM THE FLAME

As.	Sb.
Spot + heat = volatile.	Non volatile.
" + iodin = yellow AsI_3.	Orange SbI_3.
" + nitric acid soluble, forms H_3AsO_3.	Insoluble. Turns white forming Sb_2O_3.
" sodium hypochlorite solution = soluble.	
Reaction.—$3CaOCl_2 + 4AS = 2As_2O_3 + 2CaCl_2$.	Insoluble.
Reactions of the solutions.	
Arsenic solution + Sodium hydroxid = no precipitate.	White precipitate soluble in excess.
H_2S gives a yellow precipitate of As_2S_3.	Orange Sb_2S_3.
Water = no precipitate.	White SbOCl.

NOTE.—Bismuth the last element of the nitrogen family is so strongly metallic in its properties that it will be considered with the metals.

COMPARISON OF THE ELEMENTS OF THE NITROGEN GROUP.

ELEMENTS.	ATOMIC WEIGHTS.	PHYSICAL STATE.	SPECIFIC GRAVITY.	PROPERTIES.	COMMON HYDROGEN COMPOUNDS.	HALOGEN COMPOUNDS.	OXYGEN COMPOUNDS.
Nitrogen N.	14.03	Gas.	. . . .	Non-Metallic. 	NH_3 Ammonia.	NCl_3 Explosive Liquid.	N_2O NO N_2O_3 NO_2 N_2O_5
Phosphorous P.	31.	Yellow Solid.	1.82		PH_3 Phosphin.	PCl_3 liquid easily decomposed by water. PCl_5 solid. Decomposed by water	P_2O_3 P_2O_4 P_2O_5
Arsenic As.	75.	Grey Crystalline Solid.	5.7		AsH_3 Arsin.	$AsCl_3$ Liquid. Decomposed by water.	As_2O_3 As_2O_5
Antimony Sb.	120.	Silver white Crystalline Metallic Solid.	6.7		SbH_3 Stibin.	$SbCl_3$ Solid. $SbCl_5$ Liquid. Both are decomposed by water.	Sb_2O_3 Sb_2O_4 Sb_2O_5
Bismuth Bi.	208.	Reddish metallic solid.	9.8	Metallic.	------	$BiCl_3$ Solid.	BiO Bi_2O_3 Bi_2O_4 Bi_2O_5

THE CARBON GROUP OF ELEMENTS.

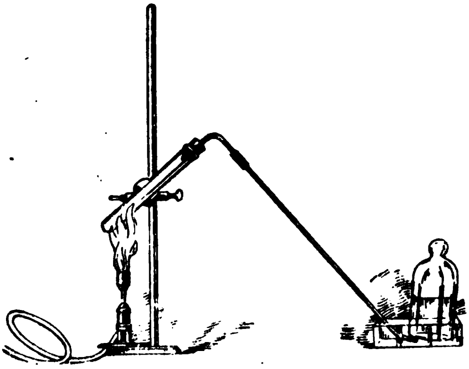
This group includes four common elements, the two nonmetals, carbon and silicon, and the metals lead and zinc.

CARBON.

Symbol, C. Atomic Weight, 12.

Carbon has been known for a very long time in its free forms but its relation to the other elements was not understood until the birth of organic chemistry in the early part of the 19th century.

Carbon is very widely distributed in nature, occurring free as Diamond, Graphite and the various forms of Coal. In the combination with oxygen and hydrogen it forms nearly all organic compounds hence is the chief constituent of all animal and vegetable organisms.



Exp. 139. Arrange a test tube with a delivery tube. Fill the tube with shavings or small

pieces of wood, and heat. Collect the gas evolved over water and test with a lighted splint. When the gas ceases to come off, close the tube with a cork and allow to cool, When cool examine the contents of the tube. What have you? Compare with charcoal. Heat a small piece of the charred wood in an iron spoon. Does it burn with flame? What causes the flame of burning wood?

Test the gas with moist litmus paper.

Exp. 140. Repeat the above using small pieces of bituminous coal. Note the tar formed. Test the gas with red and blue litmus paper. How does it differ from that made from wood? Examine the residue in the tube. What is it? Which gas burns better, that made from wood or that from coal?

Exp. 141. Place any cold object that will not be burned such as a bottle, an iron spoon, etc., for a short time in the luminous flame of the Bunsen burner. Note the black deposit. What is it?

Exp. 142. Make a mixture of one part powdered charcoal or lamp-black to eight of copper oxid (CuO) and heat strongly in a test tube. After heating some time, break the test tube and note the change that has occurred. The CuO has been reduced to metallic copper. Why?

What has become of the oxygen? Explain oxidation and reduction.

Exp. 143. Absorption of gases by carbon.

Heat a small piece of charcoal about as large

as the end of your finger. Allow to cool. Collect a test tube full of dry ammonia gas over mercury. Place the charcoal in the tube. Note that the mercury rises. Why?

Exp. 144. Absorption of organic colors by carbon.

Boil some dilute litmus solution with powdered animal charcoal or boneblack. Filter the solution after boiling and note the change. Try the same with a solution of hydrogen sulfid; with potassium dichromate. The color of an organic coloring substance is removed by carbon while that of most mineral substances is unchanged. Odors are removed also.

The above principle is used in the purification of drinking water, in the refining of sugar and in many other chemical operations.

Exp. 145. Approximate analysis of coal.

a. Powder a small sample of coal and weigh out about one gram into a crucible. Platinum is to be preferred but porcelain will do. Heat in a drying oven for an hour to 110° C., cool and weigh. The loss of weight represents the amount of moisture in the coal. To determine the per cent., multiply this loss of weight by 100 and divide by the weight of the sample, i. e.: Suppose that the loss is .0135 gram and that the weight of the sample used was 1.247, then $.0135 \times 100 \div 1.247 =$ the per cent. or 1.04 %.

b. Place the coal in the covered crucible in a good Bunsen flame for exactly five minutes. Place the crucible just above the blue inner cone of the flame. Cool and weigh and the loss will represent the volatile constituents of the coal all classed under the head of volatile hydrocarbons. Determine the per cent. as before.

c. Heat the crucible in the full flame of a blast lamp until all the carbon is burned off and the crucible contents are reduced to a perfect ash. The loss of weight this time represents the coke or fixed carbon.

d. What remains in the crucible is ash. Determine its weight by subtracting the weight of the crucible from that of crucible plus the ash.

The total percentage should equal 100%.

CARBON AND OXYGEN.

There are two compounds of carbon and oxygen, carbon monoxid (CO) and carbon dioxid (CO_2).

CARBON MONOXID.

Formula, CO. Molecular Weight, 28.

Carbon monoxid does not occur free in nature but is found wherever carbon is burned in a quantity of oxygen insufficient to produce complete combustion. It causes the blue flame of the coal stove when fresh coal is put on the fire.

Carbon monoxid is very poisonous so that all

experiments with it should be performed under a hood or in a well ventilated room.

It may be prepared in a number of ways, by the reduction of CO_2, i. e., by passing CO_2 over red hot charcoal or some other strong reducing agent, or by the decomposition of formates or oxalates.

Exp. 152. Arrange a small flask with a delivery tube. In it place about ten grams of oxalic acid $H_2C_2O_4$ and cover with concentrated sulfuric acid. Arrange to heat. On heating, CO and CO_2 will be formed. To remove the CO_2 pass the gas through a solution of potassium hydroxid in a gas washing bottle and collect the CO over water.

Reaction. Oxalic acid is decomposed by the sulfuric acid into water, CO and CO_2. The potassium hydroxid removes the CO_2 with formation of K_2CO_3 as follows:

$$H_2C_2O_4 = H_2O + CO_2 + CO.$$

$CO_2 + 2KOH = K_2CO_3 + H_2O$. The sulfuric acid removes the water.

Exp. 153. Test a bottle of CO with flame. Does it burn or support combustion?

Into a bottle of the gas pour a little $Ca(OH)_2$. Is a precipitate formed? Next ignite the gas and shake the bottle. Is the $Ca(OH)_2$ changed? What is formed by the combustion of CO?

CARBON DIOXID.

Formula, CO_2. Atomic Weight, 44.

Carbon dioxid is noted as being the first gas

to be distinguished from common air. It has been known under many different names, "chalky air," "fixed air," carbonic acid, etc. It is the choke damp of the mines.

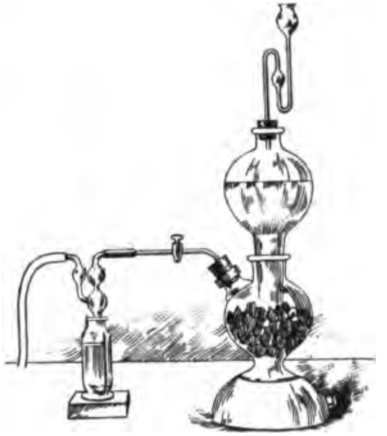
CO_2 occurs free in the atmosphere, in soils, in mineral water and because of its great weight in mines and wells. Combined with metals CO_2 forms a large portion of the earth's surface. In the form of $CaCO_3$ it occurs in all the varieties of lime stone, chalk, marble, etc. With magnesium it forms Magnesite ($MgCO_3$), with iron, siderite ($FeCO_3$), with Mg and Ca, Dolomite, etc.

In nature CO_2 is made by the combustion or decay of organic materials and by the breathing of animals.

Exp. 154. Into an empty bottle lower a glowing splint. Pour in a few drops of $Ca(OH)_2$ and shake. Note the precipitate. What is it? Write the reaction.

Exp. 155. Preparation. Arrange a generator in the same way as for hydrogen. Place in the bottle several small pieces of marble ($CaCO_3$). Cover these with water, and through the thistle tube pour small quantities of concentrated HCl. The gas may be collected over water or by downward displacement. The latter method is usually adopted. Collect several bottles full. In a bottle of the CO_2 thrust a burning piece of cotton soaked in

alcohol. Does the CO_2 burn or support combustion? Could you live in an atmosphere of CO_2?



NOTE. A Kipps apparatus may be used with good results when a large quantity of CO_2 is desired. Fill the middle bulb with marble and in the upper pour dilute HCl (one part concentrated acid to three of water) until the acid fills the lower bulb and partly covers the marble in the middle bulb. See figure of Kipps apparatus.

Exp. 156. Pass a stream of CO_2 into a solution of $Ca(OH)_2$ until the precipitate which forms at first redissolves. The white precipitate is $CaCO_3$.

Reaction.

1. $Ca(OH)_2+CO_2=CaCO_3+H_2O$.
2. $CaCO_3+H_2O+CO_2=CaH_2(CO_3)_2$, calcium acid carbonate.

Boil the clear solution thus formed. What happens? Explain the deposition of lime on the inside of a tea kettle.

Exp. 157. Place a lighted candle at the lower edge of a sloping board and pour CO_2 on the board so that it will run down onto the candle.

Pour a bottle of CO_2 onto a burning candle as you would pour a glass of water on it.

What two properties of CO_2 do these experiments illustrate?

Exp. 158. Breathe through a glass tube into a quantity of lime water—i. e. $Ca(OH)_2$ solution. What have you learned about the process of breathing from this experiment?

Exp. 159. Lower a piece of burning phosphorous into a bottle of CO_2. Note the action of the gas on flame and explain the principle of the fire extinguisher.

Exp. 160. In a bottle of air place a glowing piece of *charcoal* suspended on a wire. When the coal ceases to glow test the contents of the bottle for CO_2 by means of lime water, i. e., pour in about two c. c. of lime water and shake.

Test the air of the room by filling a large bottle with it and shaking up with lime water. To get the air from the room carefully suck out air already in the bottle with a glass tube. In sucking out the air do not breathe into the bottle. Also test the air of the room by allowing a *watch glass*

full of lime water to stand in the room for an hour or more. Note the surface of lime water. What has formed on it?

Exp. 161. Conduct CO_2 into 3 cc. of NaOH solution.

a. Evaporate a portion of the solution to dryness and compare the resulting product with a sample of Na_2CO_3. Treat with a little HCl. What gas is set free? Write the reaction.

b. To other portions of the solution add solutions of lead nitrate, zinc sulfate and manganese sulfate. Write the reactions.

CARBON AND SULFUR.

Carbon forms but one compound with sulfur, carbon disulfid (CS_2).

This was discovered in 1796 and was made by passing sulfur vapors over red hot charcoal.

Properties.

Examine a sample of CS_2. Note the play of colors in it. This is due to its high index of refraction.

Exp. 162. Place a small quantity of CS_2 in a watch glass or small evaporating dish and blow upon it through a glass tube. Place a drop or two on the hand. Note the extreme cold. What is the cause.

Bring together one cc. CS_2 with five cc. water. Note the effect.

Repeat with five cc. alcohol or ether. Note the difference.

Exp. 163. Drop a small piece of phosphorous into CS_2. Dip a piece of filter paper in the solution and allow to evaporate in the air. What is the result?

CARBON AND NITROGEN.

There is but one compound of N. and C. cyanogen CN.

This is such a poisonous substance that it cannot be handled with safety except under the most favorable conditions. It should never be made except under a hood in good working order.

Exp. 164. Preparation. Hood.

Under a hood heat a small quantity of mercuric cyanid $Hg(CN)_2$ in a glass tube. An inflammable gas will be given off. Note the color of its flame.

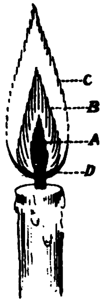
NOTE.—There are many compounds of cyanogen which are of great importance, such as ferro- and ferri-cyanids, sulfocyanids, hydrocyanic acid, etc., but these will be studied under the subject of analytical chemistry.

FLAME.

A. STRUCTURE.

I. Examine a candle flame for the four parts. A. The small blue cup-shaped portion of the flame at the base of the wick. This may be con-

sidered as merely a thick portion of the almost invisible blue mantle D. B. The more luminous cone in the very center of the whole flame. C. The more luminous cone outside the central cone. D. The nearly invisible coat that surrounds the entire flame. This last is very hard to see. Draw a very accurate diagram of the candle flame showing all the parts. The heat of combustion of the first zone A converts into a gas a large quantity of the fatty materials of the candle which are being drawn up by the wick. These gases form the second zone B. This zone is completely shut off from the air and therefore there is no combustion in it. You may prove this by putting a match head in this portion of the flame. The match will not ignite if the experiment is well performed. Make several trials. In the next portion of the flame C, the luminous cone, the supply of air is not sufficient to burn up all the gases formed. These are all compounds of hydrogen and carbon and in this zone they are partially consumed, burning to CO_2 and water, but a large part of the carbon is merely heated white hot, thus rendering the flame luminous. Outside of the luminous zone is an almost invisible coat where the gases are completely consumed. The ultimate products of all the gases burned are carbon dioxid and water.



II. Press down upon a candle flame a piece of white letter paper or some other heavy paper until it almost touches the wick. Observe the charred ring with a white center. Cause? Which is the hottest part of the flame?

III. Hold a thin wire, either iron or platinum, across a candle flame or luminous burner flame. Note where the wire is hottest. Repeat with a piece of wire gauze. Repeat with a match stub or piece of wood.

B. NATURE OF FLAME.

I. Blow out the candle,, then ignite the smoke. Why does it ignite?

II. Place a piece of wire gauze on a ring stand and turn on the gas in a burner placed under it. Now above the gauze light the gas. It will burn for some time above the gauze. Turn off the gas and allow the gauze to cool. Again light the gas, this time under the gauze. The wire gauze is such a good conductor of heat that the gas on the side opposite the flame is not heated to the point at which it will ignite. The safety lamp invented by Sir Humphrey Davy for use in coal mines is simply a lamp completely surrounded with wire gauze. This can be taken into a combustible gas and kept there for a short time without setting fire to the gas.

III. Heat a small glass tube until quite warm and at once place the end in the dark center of the

candle flame and ignite the gas at the other end of the tube. What does this show?

C. LUMINOSITY OF FLAME.

I. Stop the holes of the Bunsen burner and note the effect. Why is this? Compare color of flames when the holes are open and when they are shut. Take a burner apart and notice its construction. What is the use of allowing the air to enter the lower part of the tube and thus mix with the illuminating gas in it?

Rub two pieces of charcoal together over the blue flame and note the effect.

II. Press a cold spoon down on both burner flames and note the effect. What makes the flame luminous? Which is the hotter of the two flames? Why?

D. CHEMISTRY OF FLAME.

I. Hold a candle in a wide mouthed bottle till it goes out. Test the contents of the bottle by shaking up with lime water. One cc. is enough.

II. Hold a clean bottle over a luminous flame and note the deposit.

E. BLOWPIPE FLAME.

Close the holes in the Bunsen burner by turning the tube. Obtain the oxidizing flame by placing the blowpipe tip inside the dark portion of the flame just over the top of the burner, and blow across the flame somewhat

strongly. An almost colorless pointed flame is produced. The reducing flame is obtained by placing the tip a little higher above the burner top and outside the flame. A luminous flame is produced. Which is hotter? Why?

The reducing flame is luminons because it contains hot carbon. Hot carbon combines with oxygen with great energy, hence its presence explains the reducing action.

CARBON AND HYDROGEN.

Carbon and hydrogen have the power of satisfying their valence by combining one with the other. Because of this property they are capable of forming an almost infinite number of combinations. These compounds are called hydrocarbons. A complete discussion of them belongs to the subject of organic chemistry.

The hydrocarbons fall into several groups which differ from each other by the increment CH_2. The three chief groups may be represented by the general formulas CnH2n+2 (the Methane Group), CnH2n (the Ethylene Group) and CnH2n—2 (The Acetylene Group). We need only to discuss the most common of each group. These are Methane (CH_4), Ethylene (C_2H_4) and Acetylene (C_2H_2).

METHANE.

Symbol CH_4. Molecular weight 16.

Methane has been known for a very long time

but was not distinguished from hydrogen, which it resembles in many ways, until late in the 18th century. At that time it was found that it required a greater volume of oxygen for its combustion than hydrogen and that the products of combustion were different.

Methane is formed in nature by the decomposition of vegetable matter, usually under water. It is found in marshes and in coal mines where it is known as "marsh gas" and "fire damp." It is the chief constituent of natural gas.

Exp. 165. Fit a tube of hard glass or iron with a stopper and delivery tube and in it heat a mixture of four parts soda lime with one part of sodium acetate ($NaC_2H_3O_2$). Soda lime is a mixture of quick lime (CaO) with sodium hydroxid ($NaOH$). Collect several jars of the gas over water. Apply a flame to the contents of one of the jars holding the jar with its mouth turned upwards. Repeat with another with the mouth down. What is the weight of methane as compared with air? Note the color of the methane flame. Into a jar in which methane has been burned pour a few drops of lime water. Note the precipitate formed. Cause? Write the reactions for the burning of methane.

Reaction for the formation of methane.

$$NaC_2H_3O_2+NaOH=Na_2CO_3+CH_4.$$

Exp. 166. Into a bottle of methane pour a few

drops of chlorin water. Cover and shake. Note the odor of the product formed. This is chloroform, the well known anaesthetic ($CHCl_3$). Write the reaction.

ETHYLENE.

Formula C_2H_4. Molecular weight 28.

Ethylene was discovered in the 17th century although its composition was not determined until later.

Ethylene occurs in small quantities in natural gas and is the chief constituent of the gas formed by the distillation of coal, i. e., illuminating gas. It is also known as olefiant gas or ethene.

Exp. 167. Into a test tube arranged with stopper and delivery tube pour a mixture of two cc. alcohol (C_2H_5OH) and eight cc. concentrated sulfuric acid. Extreme care must be used in mixing alcohol and acid as much heat is developed. Pour the acid slowly into the alcohol, stir vigorously, and cool by holding the test tube in cold water.

Heat the mixture gently and collect the gas (C_2H_4) over water. The mass in the test tube will become black and will froth violently if the heating is too rapid.

Test a jar of the gas to see how it will burn. Force the gas out of the bottle by pouring in water as fast as it burns. How does the weight of ethylene compare with that of methane? Write the reactions for the combustion of ethylene.

Reaction for the formation of ethylene.

$$C_2H_5OH=C_2H_4+H_2O.$$

The sulfuric acid has a strong affinity for water and forms C_2H_4 from the alcohol by taking away its water.

Several other reactions take place, for example the sulfuric acid is reduced forming SO_2. Hence this gas is mixed with the ethylene.

Exp. 168. Into a jar of ethylene pour a few drops of sodium hydroxid solution and shake. This will remove any SO_2 which might be mixed with the gas. Next pour in a little bromin water and shake again. Note the odor of the product formed. This is ethylene dibromid ($C_2H_4Br_2$). Note the oily form of the dibromid. The name olefiant gas which is sometimes applied to ethylene is due to its propensity of forming heavy oily liquids with the halogens and other elements.

ACETYLENE.

Formula C_2H_2. Molecular weight 26.

Discovered in the early part of the 19th century but was first investigated by Berthollet in 1859.

Acetylene is the only hydrocarbon which has been made by direct synthesis of its elements. It may be made by passing a powerful electric current through carbon electrodes in an atmosphere of hydrogen. It is more commonly made from calcium carbide (CaC_2). Calcium carbide is prepared by fusing together lime and carbon in an electric furnace.

Exp. 169. Throw a small piece of calcium carbide into water. Light the gas generated. Note the flame and odor of the gas. How does the flame differ from that of the other hydrocarbons that you have studied? How may acetylene be used for purposes of lighting?

Exp. 170. Fill a small jar with water and invert in a dish of water. Hold a small piece of calcium carbide wrapped in wire gauze under the mouth of the jar. Into the jar of gas thus collected pour a little cuprous chlorid solution which has been made strongly alkaline with ammonia. Note the precipitate formed. This is copper acetylide $C_2H_2Cu_2O$.

Reactions.

$Cu_2Cl_2(NH_3)_2 + H_2O + C_2H_2 = 2NH_4Cl + C_2H_2$
Cu_2O.

Exp. 171. Allow an old Bunsen burner to burn at the base of its tube, i. e., "to strike down." Note the odor of the gas formed. What is it?

CARBON AND THE HALOGENS.

Carbon and the halogens do not unite directly. If certain of the hydrocarbons are treated with chlorin part or all of their hydrogen will be replaced. This is true in a degree of the other halogens. For example:

$CH_4+Cl_2=CH_3Cl$(monochlor methane)$+HCl$.
$CH_3Cl+Cl_2=CH_2Cl_2$(dichlor methane)$+HCl$.
$CH_2Cl_2 + Cl_2 = CHCl_3$ (trichlor methane or

chloroform)+HCl.

$CHCl_3+Cl_2=CCl_4$(tetrachlor methane or carbon tetrachlorid)+HCl.

Experiments with the halogen compounds of carbon are somewhat difficult and belong more properly to organic chemistry.

ALCOHOL.

The alcohols are compounds of carbon, hydrogen and oxygen. They form a very important class. The most common is ethyl alcohol or grain alcohol as it is sometimes called. This has the formula C_2H_5OH.

Exp. 172. Fit a 500 cc. flask with a rubber stopper having one hole. Fit a short glass tube to the stopper and connect the flask by means of a rubber tube to the longer tube of a gas washing bottle which contains a few cc. of calcium hydroxid solution.

In the flask place a solution of 200 grams of grape sugar in 400 cc. water. Introduce a piece of fresh, compressed yeast and allow to stand in a moderately warm place. After twenty-four hours examine the liquids in the flask and in the wash bottle. Note the precipitate in the $Ca(OH)_2$ solution. What is it? Note that the sugar solution is no longer clear.

After the flask has been allowed to stand about two days connect it with a condenser (see experi-

ment on distillation) and distil on a waterbath. Examine the distillate. Note the odor. Taste of a drop. Test the liquid to see if it will burn.

SILICON.

Symbol, Si. Atomic weight, 28.4.

Silicon is very widely distributed in nature, making up over 27% of the earth's crust. It never occurs free but in the form of the oxid SiO_2 (silica), in combination with metals as silicates, etc. In the form of its oxid it occurs in a comparatively free state as quartz, flint, etc. Sand is silica mixed with many impurities. Feldspar and mica are silicates. These with silica are the principal ingredients of such rocks as granite, syenite, etc., and form a large part of the earth's crust.

Preparation.

Exp. 173. Mix 6 grams of powdered Mg with about four times the quantity of powdered sand. Place the mixture in a wide test tube of hard glass and heat in a blast lamp. The metal will combine with sand with almost explosive violence. When cool treat the residue in the tube with dilute HCl to free the silicon from magnesium oxid which is one product of the reaction. That which remains after the magnesium oxid has been removed is a mixture of sand and free silicon.

Examine the silicon. Test its solubility in H_2SO_4, HNO_3, HCl and KOH or NaOH.

Reaction, $SiO_2+2Mg=2MgO+Si$,

SILICON AND OXYGEN.

Silicon dioxid (silica) SiO_2.

Exp. 174. Test its solubility in the common acids and in KOH. Fuse a mixture of 1g. powdered sand with 4g. Na_2CO_3 in a platinum crucible. If platinum is not available porcelain may be used, although the experiment will probably ruin it. When cool dissolve the resulting compound in water. Sodium silicate Na_4SiO_4 has been formed. Sometimes this is called waterglass or soluble glass.

Exp. 175, To a portion of the silicate add HCl. What is formed? Evaporate to dryness. Dissolve the residue as much as possible in water and filter out the precipitate. What is this precipitate?

Exp. 176. Bend a loop in a platinum wire and in the loop make a bead of microcosmic salt $(NH_4)NaHPO_4$. Dip the bead into a powdered quantity of sand and test in a blowpipe flame. What happens?

GLASS.

Glass is the most important artificial compound of silicon. It is made by firing together sand, a metallic oxid and and a carbonate of one of the alkali metals, as K_2CO_3 or Na_2CO_3. The chief metallic oxids are CaO, PbO and Fe_2O_3. The properties of the glass depend upon the kind of metallic oxid and the kind of carbonate used.

THE ELEMENTS OF THE CARBON FAMILY.

There are five elements which show many characteristics in common with carbon. These are placed in a group called the carbon family.

The elements in the group are the two nonmetals carbon and silicon and the metals germanium, tin and lead. Other metals are frequently classed with these also. Tin and lead will be described under the subject of metals.

COMPARISON OF CARBON AND SILICON.

Symbol.	Atomic weight.	Compounds with H.	Compounds with O.	Compounds with S.	Chlorids.
Carbon, C	12	CH_4	CO CO_2	CS_2	CCl_4
Silicon, Si	28	SiH_4	SiO_2	SiS_2	$SiCl_4$

There are many compounds of carbon and hydrogen, except CH_4, but no other in which there is but one carbon atom.

BORON.

Symbol, B. Atomic weight, 10.86.

Boron in its physical properties is very much like carbon although the chemical compounds which it forms place it in the nitrogen family. Boron does not appear free in nature, but is found in combination with hydrogen and oxygen as boric and boracic acid H_3BO_3 and in combination with sodium as borax, $Na_2B_4O_7$.

Preparation.

Exp. 177. Boron may be prepared by a meth-

od similar to that given for silicon. Fuse a small quantity of ordinary borax. When cool pulverize and mix with about one half as much powdered magnesium. Heat in a hard glass tube with a blast lamp. Dissolve out the unused borax and the magnesium oxid with hot water containing a little hydrochloric acid. Filter and dry the boron. Examine, test its solubility in acids and alkalies and compare with silicon.

COMPOUNDS OF BORON.

Boric acid, H_3BO_3.

Exp. 178. Preparation.

Dissolve half a test tubeful of borax in 10 cc. of boiling water in a beaker or small evaporating dish and add to the solution 2.5 cc. of concentrated hydrochloric acid. As soon as the solution cools crystals of boric acid will be deposited on the bottom of the dish.

Exp. 179. Test for boric acid.

Dissolve a little of the boric acid you have made in alcohol in an iron spoon. Ignite the alcohol and stir the burning solution with a glass rod. The flame will be colored green. A compound called ethyl borate is formed.

Exp. 180. To make boric anhydrid (B_2O_3). In a clean iron spoon heat some crystals of boric acid. When the water has all been driven off, the anhydrid will be left as a clear liquid which may

be drawn out in long threads by touching to the surface of the liquid a stick or glass rod. When cold the anhydrid will resemble glass.

PROBLEMS.

1. How much CO_2 will result from the combustion of 20g. of C?

2. What volume of carbon dioxid will be set free when a quantity of $CaCO_3$ is treated with 10g. of HCl containing 20% pure HCl gas, if CO_2 weighs 22 times as much as hydrogen?

3. How much oxalic acid would be necessary to set free 50g. of CO?

4. How much boric anhydrid can be made from 10g. borax ($Na_2B_4O_7 10H_2O$)?

BLOW-PIPE ANALYSIS

Generally to determine the constitution of an unknown substance it is first dissolved in some solvent. The process of solution often makes a complete change in the nature of the substance and to know its original character we must analyze it in the dry state.

The nature of any simple substance may be made manifest by subjecting it to several operations, such as heating it in a glass tube, fusing it on charcoal, determining the color it will give when heated in a Bunsen flame, etc.

As all simple inorganic substances and many organic compounds may be completely analyzed in the dry state the subject of blow-pipe analysis is one of great importance.

In the following text only the more common facts are stated. Extremely poisonous substances and those that are very rare have been purposely omitted as beyond the scope of the ordinary student.

The text is given in the form of a scheme for the analysis of unknown substances, but it is recommended that the student should go through all the processes first with known substances and verify each reaction before the unknowns are attempted. In the author's own laboratory students have been required to analyze a series of fifty unknowns which has been found sufficient to fix all the facts firmly in mind.

Nearly all of the reactions are produced by the use of heat alone or by the combined action of heat and reagents. For the heating we use an ordinary Bunsen lamp and a blow-pipe. For obtaining the best results with the blow-pipe a tube is inserted in the lamp which makes the flame broad and luminous. This tube is of brass, of a size so as to fit into the burner tube exactly. The end is hammered flat so that the opening is as long as the breadth of the burner tube and about one-fifth as wide. The inner tube is filed off so as to have an angle of about 30 degrees.

The blow-pipe is used for obtaining both an oxidizing and a reducing flame. To produce the first, turn down the Bunsen flame until it is about an inch long, place the tip of the blow-pipe inside the flame near the top of the burner and blow rather strongly. A pointed blue flame is obtained. The reducing flame may be obtained by placing the blow-pipe tip outside the upper part of the flame. This is a pointed luminous flame containing incandescent carbon, hence its reducing power.

When a solid substance is heated it will undergo one or more of about six changes. It may

a. Give up water.
b. Give off a gas.
c. Form a sublimate, colored or white.
d. Change in color.
e. Fuse without decomposition.
f. Carbonize, i. e., blacken.

If the substance suffers one or more of these changes we will gain a clue to its identity at once.

The heating takes place in a little tube about three inches long, made of hard glass and closed at one end. The tube should not be more than one-fourth inch in diameter.

I. THE SUBSTANCE IS HEATED IN A GLASS TUBE.

A. WATER IS GIVEN OFF.

1. The substance may be a deliquescent salt, i. e., one which absorbs water from the air. The quantity of water is usually large and it is given off at a low temperature. Such a salt is calcium chlorid ($CaCl_2$).

2. The substance may contain enclosed water. Such salts snap or decrepitate when heated. Decrepitation is best shown by the salts of the alkali metals with the halogen acids. Such are potassium and sodium chlorids, bromids and iodids.

3. The substance may contain chemically combined water. Usually a high temperature is re-

quired to drive it off and it often shows a characteristic reaction with litmus paper. The water may be acid in which case the original substance may have been an acid salt or it may be alkaline and the substance a hydroxid or ammonium compound.

Organic compounds char and give off odors like those of burning wood. The amount of water in a salt in which it is chemically combined is usually small.

4. May contain water of crystallization. The quantity is quite large and many substances swell up greatly in giving off their water of crystallization. Such are alums, borates and phosphates.

B. A GAS IS GIVEN OFF.

This may be one of the following:

1. Oxygen.

Introduce into the tube a splinter of wood on which there is a spark of fire. The oxygen will cause the splinter to ignite. Oxygen indicates that the substance was a peroxid, nitrate, chlorate, bromate, iodate, dichromate or permanganate.

2. Nitrous oxid (N_2O).

This supports combustion nearly as well as oxygen. Thus the same test may be used to recognize it. Nitrous oxid indicates ammonium nitrate. Ammonium nitrate when heated undergoes decomposition with a series of little explosions especially if heated rapidly, thus we may distinguish the substance from one which gives oxygen.

3. Ammonia (NH_3).

Indicates ammonium compounds. It may be identified by the odor and by the fumes of ammonium chlorid which it forms when a stopper wet with hydrochloric acid is held at the mouth of the tube.

4. Carbon dioxid (CO_2).

Indicates a carbonate or organic compound. Carbon dioxid may be recognized by passing it into a solution of lime water $Ca(OH)_2$ which will be colored white by a precipitate of $CaCO_3$.

The best method of testing for CO_2 is to attach to the tube in which the carbonate is heated, a glass tube drawn out to a capillary and bent like a siphon. The two tubes are attached by a rubber tube. The siphon capillary is dipped into the lime water solution and the other tube is heated.

5. Carbon monoxid (CO).

Indicates an oxalate or a formate. The gas burns with a bright blue flame when pure. Often the nature of the salt changes the flame color.

The formates blacken when heated leaving a residue of carbon. The oxalates on the contrary decompose into CO_2 and CO, so have no residue.

6. Sulfur dioxid (SO_2).

Indicates a sulfate or sulfite. It is recognized by its odor which is that of burning sulfur.

7. Hydrogen sulfid (H_2S).

Indicates a sulfid containing water. It may be identified by its odor and by the blackening of a piece of paper wet with lead acetate held in the gas..

8. Nitrogen trioxid or tetroxid(N_2O_3 or N_2O_4).

Indicates a nitrate or nitrite of a heavy metal such as lead, mercury, etc. The alkaline salts do not give this reaction. The reddish brown gas can be best seen by looking through the glass tube lengthwise at a white surface.

9. Chlorin (Cl).

Indicates certain chlorids such as anhydrous magnesium chlorid ($MgCl_2$), and certain hypochlorites.

10. Bromin (Br).

Indicates certain bromids. Is identified by its odor and the red brown color of its vapor.

11. Iodin (I).

Recognized by the violet color of its vapor. Its odor is much like that of bromin. Indicates free iodin and such iodids as CdI_2, HgI_2, MgI_2, AuI, etc.

12. Cyanogen. POISON. Work under a hood.

Indicates a cyanid of one of the less basic metals, such as mercury, etc. Is identified by its flame which when pure is of a crimson color. Cyanogen has an odor like potassium cyanid (KCN).

NOTE—Cyanogen and its compounds are too dangerous for the ordinary student. They should never be handled except under a skillful teacher and in the most favorable laboratory conditions.

13. Acid fumes.

Indicate certain sulfates and sulfites of weak bases. Such a compound is $Fe_2(SO_4)_3$. The fumes are detected by their action on litmus paper.

C. A SUBLIMATE IS FORMED.

I. White.
II. Colored.

Many solid substances when heated pass directly into the gaseous state. When the gas reaches a cool part of the receptacle in which it has been heated it will condense and in this condensed form is known as the sublimate.

The following give:

I. WHITE SUBLIMATES.

a. Ammonium compounds.

To determine an ammonium compound exactly place a little of the substance in a test tube with concentrated sodium hydroxid and heat. Ammonia will be set free which may be recognized by the odor.

b. Arsenic trioxid (As_2O_3).

Gives a sublimate of octahedral crystals. These are very small so that a magnifying glass must be used to see their form. Mix the substance with a little charcoal and heat. A black mirror of metallic arsenic will be formed.

c. Antimony trioxid (Sb_2O_3).

This volatilizes at a very high temperature, 1600 degrees C. forming a sublimate of needle shaped crystals.

d. Mercurous chlorid ($HgCl$). HOOD.

The sublimate is yellow when hot and white when cold.

e. Mercuric chlorid ($HgCl_2$).

This acts much like the mercurous compound except that it melts before it sublimes.

II. COLORED SUBLIMATES.

a. Arsenic. HOOD.

Gives a shining black mirror. This is formed by the element itself or by its compounds in combination with some reducing agent. Arsenic has a peculiar odor like that of garlic.

b. Arsenious sulfid (As_2S_3).

The sublimate is reddish brown when hot and yellowish red when cold.

c. Antimony sulfid (Sb_2S_3).

Sublimes at a high temperature. The sublimate is black when hot and reddish brown when cold.

d. Mercuric sulfid (HgS).

Gives a black sublimate when hot which is red when rubbed with a glass rod.

e. Mercuric iodid (HgI_2).

Forms a yellow sublimate which changes to red.

f. Iodin.

Forms a purple vapor and a black sublimate.

g. Sulfur.

The sublimate is yellow. It indicates free sulfur or certain sulfids such as FeS_2. It burns with a blue flame with the characteristic odor of sulfur dioxid.

D. THE SUBSTANCE CHANGES COLOR ON HEATING.

Many substances especially metallic oxids which do not decompose or sublime on heating will change color. The most characteristic changes are as follows:

1. Zinc oxid (ZnO).

Is white when cold and changes to a yellow on heating then becomes white again on cooling.

2. Stannic oxid (SnO_2).

The original substance is white when cold, becomes yellow brown when hot and pale yellow on cooling.

3. Lead oxid (PbO).

Is brownish yellow when cold, becomes red when hot and yellow on cooling. It fuses at a high temperature.

4. Bismuth oxid (Bi_2O_3).

Yellow when cold changing to orange yellow on heating and is yellow again when cold. It fuses at a high temperature.

5. Mercuric oxid (HgO).

Yellowish red, becomes black or dark brown when hot and red on cooling. It decomposes readily giving off oxygen and a black sublimate of mercury. The mercury often deposits on the sides of the tube to form a mirror much like that of arsenic.

6. Ferric oxid (Fe_2O_3).

Red or brown and changes to black but becomes red again on cooling.

NOTE—The above results are given as if for oxids alone but all salts which decompose readily into oxids give the same reactions.

E. THE SUBSTANCE FUSES WITHOUT DECOMPOSITION.

This usually indicates a salt of the alkali metals such as potassium or sodium. Some other salts fuse, hence this is not a sure test for the alkalies.

F. THE SUBSTANCE BLACKENS.

This usually indicates an organic compound. Nearly all organic compounds on being heated decompose, setting carbon free. At the same time gases are given off which have a characteristic odor. The most common organic compounds which can be recognized by the blow-pipe are:

1. Acetates.

When heated give the odor of acetone $(CH_3)_2CO$ which smells like vinegar. Acetone burns with a blue flame. Do not confuse it with CO which is given off by formates.

2. Formates.

Give off carbon monoxid which burns with a blue flame. Often the color of the flame is modified by the metal of the salt. Thus sodium formate will give CO which burns with a yellow colored flame.

3. Tartrates.

When heated have an odor much like that of burnt sugar.

NOTE—The alkali salts with the organic acids on heating form carbonates, while all other metals form first carbonates then finally oxids of the metals.

II. THE SUBSTANCE IS HEATED ON CHARCOAL.

Charcoal is a very strong reducing agent when heated to incandescence and will reduce most metals in combination to the metallic state.

To heat, dig a little hole in the charcoal, fill with the substance and heat with the blow-pipe, gently at first and then more strongly. If the substance is very light and blows away wet it with water or fuse with a bit of borax. Water is preferable.

a. The Substance Fuses Easily Without Decomposition.

Indicates a salt of the alkali metals or some of the alkaline earths.

b. The Substance Gives a Metallic Bead Without an Incrustation or Coating on the Charcoal.

By the incrustation we mean the white or colored coating that forms on the cool charcoal around the bead. This is usually an oxid of the metal which has been volatilized and again condensed.

1. A white bead.

Indicates tin, aluminum or silver. These metals may be distinguished by the difference in their fusibility.

a. Tin melts at 232° C.

b. Aluminum melts at 655°.

c. Silver melts at a high temperature, i. e., 960°.

2. A red bead.

Indicates copper. This requires a very high temperature and a long continued heating. The bead is malleable. CuO also gives a red bead but it is brittle, thus it can be distinguished from metallic copper.

3. A yellow bead.

Indicates gold. To melt gold a very high temperature is necessary, i. e., 1061°.

c. The Substance Forms a Bead With an Incrustation.

1. Lead.

Gives a soft, malleable bead. The incrustation is yellow and volatile.

2. Cadmium.

Bead soft and malleable. Incrustation red brown and volatile.

3. Zinc.

Bead is white, hard and rather brittle. The incrustation is yellow when hot and white when cold. See D. 1.

4. Antimony.

The bead is white, hard and brittle. The incrustation is white and volatile.

5. Bismuth.

The bead is white, hard and brittle while the incrustation is yellow and volatile.

d. The Substance Is Infusible and Dark in Color.

Indicates iron, chromium, manganese, nickel or cobalt. All of these are more or less attracted by the magnet. They may be distinguished by the borax or microcosmic bead. See section V.

Many of the rare metals such as platinum, molybdenum and tungsten are found here. They are not at all magnetic.

e. The Substance Burns Up or Deflagrates.

This indicates a nitrate, chlorate or some other substance containing oxygen which is given up easily. The salts of the alkali metals show this reaction best.

f. The Substance Decrepitates or Crackles on Heating.

Indicates a salt containing water inclosed in the crystals. Such are the halogen compounds of the alkalies.

g. The Substance Volatilizes.

a. Those substances which form a sublimate in the closed tube will volatilize on charcoal. They will usually give an incrustation on the charcoal like that formed in the tube.

b. Arsenic. POISON. HOOD.

Forms a white incrustation which is very volatile and has an odor like garlic.

NOTE—Arsenic is very poisonous and when the student notices this garlic odor the work should be continued under a hood. It is well for the instructor to mark all poisonous substances as such so that the student may have warning.

h. The Substance Burns.

This indicates:

1. A metal.

Iron burns with brilliant sparks when finely divided leaving a residue of Fe_2O_3.

Magnesium burns with a bright flash and leaves a white residue of MgO.

2. Sulfur.

Burns with a blue flame having the odor of SO_2.

i. The Substance Is White, Infusible and Luminous When Very Hot.

Allow to cool and add a few drops of cobalt nitrate and heat again. On cooling the following substances may be indicated:

1. A blue color.

Indicates Al_2O_3, SiO_2 and certain silicates, borates and phosphates, such as those of the alkali metals.

2. A pink or flesh color indicates MgO.

3. Yellow green indicates ZnO.

Blue green " SnO.

Dark green " Sb_2O_3.

4. Violet.

Indicates a borate, phosphate or arsenate of magnesium.

5. Red brown when hot and light brown when cold.

Indicates barium. Moisten the residue with water and test with red litmus paper. It will give an alkaline reaction.

6. Gray.

Indicates a compound of calcium or strontium. The residue will give an alkaline reaction with moist litmus paper.

NOTE—Any of the above metals will give the same reactions if they are in salts which will change to oxids on heating.

III. HEAT THE SUBSTANCE ON CHARCOAL WITH SODIUM CARBONATE.

Often a metal cannot be obtained from its salts with free access to air. To exclude the air and hasten the reduction the substance may be mixed with sodium carbonate. Hence if no metallic bead is obtained with the tests under II, b and c, heat with sodium carbonate.

1. Sulfur test.

Sulfur in the form of sulfates does not readily react to form compounds by which its identity may be established. If any sulfur compound is heated on charcoal with sodium carbonate it will be reduced to sodium sulfid. This if placed on a silver coin and moistened will produce a black stain of silver sulfid. This test merely indicates that the original substance contained sulfur, but does not show whether it was a sulfate, sulfite, hyposulfite, sulfocyanid or other compound. For special tests see sections VII and VIII.

2. The magnesium test for sulfur.

Heat a small quantity of the substance supposed to contain sulfur with a little powdered magnesium in a small tube. A slight explosion will take place with formation of magnesium sulfid. Allow to cool and then add a little water. Hydrogen sulfid will be set free. See tests for phosphates section VIII.

IV. THE SUBSTANCE IS HEATED ON PLATINUM WIRE IN A COLORLESS FLAME.

Many substances when heated in a flame give to it a characteristic color. This is true particularly of the alkalies and the alkaline earths such as barium, calcium and strontium.

The substance to be heated is first put into solution or made into a thin paste with water or a little hydrochloric acid. A loop is bent in a platinum wire, dipped in the solution and held in the flame. The following are characteristic :

1. A yellow flame.

Indicates sodium. Sodium is present in small quantities in nearly all compounds so it will often obscure the characteristic flame of other metals. The yellow color will disappear if viewed through a piece of blue glass.

2. A violet flame.

Indicates potassium. The flame is visible through blue glass so can be detected in the presence of sodium.

NOTE—Arsenic, antimony and lead are often confused with potassium. If the student has any difficulty in making the distinction when working on an unknown substance, a comparison with the known material should be made to be sure of the difference in flame color.

3. A red flame.

Bright red indicates lithium.

Carmine red indicates strontium

Orange red indicates calcium.

4. A green flame.

Yellow green indicates barium or boric acid.

The latter has a soapy feeling when rubbed between the fingers, hence may be readily distinguished from the barium.

B_2O_3 will give its flame best if moistened with H_2SO_4.

Emerald green indicates copper.

Grass green indicates thallium. Rare.

A blue green flame of short duration indicates phosphates. The reaction is best shown if the sample is moistened with H_2SO_4.

5. A blue flame.

Indicates copper chlorid, lead, arsenic or antimony. The last three substances will corrode the platinum wire.

V. THE SUBSTANCE IS HEATED IN A BEAD OF BORAX OR MICROCOSMIC SALT.

A small loop is bent on a platinum wire, the wire is heated and plunged into borax or microcosmic salt and heated further until the bead becomes transparent. For most purposes both borax and microcosmic salt will act equally well. It is a little more difficult to keep the latter on the wire so the borax is generally used.

After the bead is prepared dip it while still warm into the substance to be tested. Care must be taken not to get too much. The following give characteristic tests.

Use the oxidizing flame.

HOT.	COLD.
1. Iron.	
Yellow to deep red.	Yellow to colorless.
2. Cromium.	
Yellow to green.	Grass green.
3. Nickle.	
Red.	Brown.

4. Cobalt.	
Blue.	Blue.
5. Manganese.	
Reddish violet or amethyst.	Amethyst.
6. Copper.	
Blue green.	Blue green.
7. Bismuth.	
Yellow.	Colorless or opalescent
8. SiO_2.	

Dissolves in the borax bead but in the microcosmic salt it is insoluble and forms an opaque mass which floats about in the bead. This is sometimes called the "silica skeleton."

NOTE—There is some difference if the reducing instead of the oxidizing flame is used. These tests with the oxidizing flame alone are sufficiently characteristic to identify most of the metals.

VI. THE SUBSTANCE IS FUSED ON PLATINUM FOIL WITH KNO_3 AND Na_2CO_3.

This test identifies the salts of chromium and manganese. They have been already indicated in the tests given, so fusion on foil simply confirms previous tests.

1. Chromium.

When a chromium compound is fused with Na_2CO_3 and KNO_3 it will be oxidized to a chromate which appears as a yellow residue on the foil.

To confirm, dissolve the chromate in hot water, add acetic acid to neutralize the Na_2CO_3, then precipitate the chromate with lead acetate. Yellow lead chromate will be formed.

2. Manganese.

By fusion under the above circumstances manganese compounds are changed to manganates which appear as green deposits on the foil. Treat this green deposit with boiling water and it will be decomposed, setting free brown manganese dioxid.

VII. TESTS FOR ACID RADICALS.

The substance is dropped into concentrated sulfuric acid which has been heated to about 100°. Heat one cc. of concentrated acid about as hot as can be held in the hand. This will be near 100°. Heating any hotter will decompose the acid and confuse the results. The acid is heated thus because many compounds form explosive gases when dropped into sulfuric acid and if it is hot these will decompose as fast as formed, so a dangerous explosion cannot occur.

Hot sulfuric acid will decompose nearly all salts, setting free their acid radicals. There are exceptions however. Hence when a salt and hot acid are brought together a reaction will generally occur which will tell us the nature of its radical.

1. No reaction.

Indicates sulfates arsenates, phosphates and many oxids. See special tests, section VIII.

2. Hydrogen.

Burns with a colorless flame. It indicates a free metal. Mixed with air it forms an explosive mixture. Thus it usually ignites with a slight explosion. The hydrogen is a strong reducing agent so it may reduce the hot sulfuric acid to SO_2. See SO_2. If SO_2 is obtained with concentrated acid repeat the experiment with the dilute.

3. Oxygen.

Indicates some highly oxidized compound such as peroxids, permanganates, chlorates, etc.

4. Carbon dioxid.

Indicates a carbonate, oxalate or some organic compound which is easily decomposed by H_2SO_4. Organic compounds generally blacken with hot sulfuric acid as they do when heated alone. They give off odors like burnt sugar. The carbon dioxid may be recognized by decanting the gas, which is heavier than air, into a test tube in which there is a small quantity of calcium hydroxid. A white precipitate will be formed.

5. Carbon monoxid.

Burns with a blue flame. Indicates a formate, oxalate, cyanid, ferro- or ferri-cyanid or certain organic compounds. Oxalates decompose with sulfuric acid to form both carbon monoxid and dioxid.

6. Hydrochloric acid.

Has a sharp odor. It gives white fumes with ammonia. Indicates a chlorid. Hydrobromic and nitric acids may be confused with hydrochloric. To distinguish, add a little manganese dioxid and chlorin will be set free which may be recognized by its yellow green color.

7. Hydrobromic and hydroiodic acids.

Both give white fumes with ammonia. Both have a sharp odor like hydrochloric acid. They may be easily identified however as they decompose slightly with the hot acid and set free bromin and iodin. To confirm add a little manganese dioxid and heat. Large quantities of bromin and iodin will be formed.

8. Hydrofluoric acid. HF.

Is a colorless fuming gas with a very sharp odor much like that of the other halogen acids. It is very dangerous to inhale so must be made in very small quantities. It dissolves nearly all substances including glass so it may be identified by placing a piece of glass over the mouth of a test tube in which it is being generated. Allow to stand for several hours and the glass will be etched even if the quantity of acid was very small.

9. Hydrocyanic acid. POISON.

Recognized by its odor which is like that of KCN. Given also by dilute acid. It burns with a crimson flame. It indicates a cyanid, sulfocyanid, ferro- and ferri-cyanids.

NOTE—The cyanids are such dangerous bodies that the student should not be allowed to work with them without having a full knowledge of their character.

Hydrocyanic acid is known in medicine in the form of a very dilute solution under the name of Prussic acid. It is one of the most powerful poisons known.

10. Hydrogen sulfid.

Indicates a sulfid. It may be recognized by its odor. Dilute acid also gives the reaction.

NOTE—A powerful reducing agent such as free iodin will sometimes reduce concentrated sulfuric acid to H_2S.

11. Sulfur dioxid.

Indicates a sulfite or thiosulfate. The thiosulfate gives a precipitate of free sulfur also. Sulfites and thiosulfates are decomposed by dilute as well as concentrated sulfuric acid.

Copper, lead, mercury, carbon and many other reducing agents when heated with concentrated sulfuric acid reduce it to SO_2. The dilute acid is not reduced.

12. Nitrogen peroxid.

Is a reddish brown gas. Indicates a nitrate or nitrite. The nitrites are decomposed by dilute acid while the nitrates require the concentrated.

13. Nitric acid.

Indicates a nitrate. The acid has much the same properties as the halogen acids, i. e., has a sharp odor, will fume with ammonia, etc. Introduce a small piece of copper and red fumes of NO_2 will be set free.

14. Chlorin.

Indicates a hypochlorite. It is formed also by dilute acids.

15. Chlorin peroxid Cl_2O_4.

Is a heavy gas of yellow green color which has an odor somewhat like that of a mixture of chlorin and ozone. It is very explosive, decomposing readily into chlorin and oxygen. Hence when a chlorate is dropped into hot sulfuric acid it will snap and crackle in a furious manner. In the hot acid the Cl_2O_4 decomposes as fast as formed. If the acid were not hot, enough of the gas might accumulate to cause a very dangerous explosion.

16. Bromin and iodin.

Indicate bromids and iodids.

17. Acetic acid.

May be recognized by its vinegar-like odor. Add a little alcohol to the mixture of acetate and hot acid and a pleasant apple-like odor of ethyl acetate will be noticed. (Ethyl acetate has the formula $CH_3COOC_2H_5$.)

VIII. SPECIAL TESTS.

1. Sulfates.

Give no reaction with sulfuric acid. If sulfur was found by the test under III and there is no reaction with sulfuric acid the substance is a sulfate.

NOTE—With sulfuric acid sulfites give SO_2, sulfids give H_2S and thiosulfates give both S and SO_2.

2. Sulfocyanids.

With sulfuric acid give both HCN and free sulfur. See VII, 9.

3. Boric acid and borates.

If placed in concentrated sulfuric acid with a little alcohol and warmed will form ethyl borate which burns with a green tipped flame.

4. Phosphoric acid and phosphates.

Heat the substance with powdered magnesium in a small glass tube. Use small quantities. There will be an energetic combination with the formation of magnesium phosphid Mg_3P_2. If the phosphate contained water phosphin (PH_3) will be formed which may be recognized by its odor which is like that of rotten fish. If no odor of phosphin is noticed at once, allow to cool and add a drop or two of water. If the quantity of phosphin is great it will take fire spontaneously.

NOTE—Hypophosphites when heated alone will give phosphin.

5. Oxids.

Most of the common oxids give no reaction with hot sulfuric acid, so when a substance gives no reaction with acid and is not a sulfate, borate or phosphate it is probably an oxid.

THE METALS AND THEIR REACTIONS.

There are in all about 40 elements recognized as metals in distinction to non-metals, but of these only 23 are common enough to be worth our study. Arsenic although a non-metallic element is generally classed with the metals for purposes of analysis.

In the following pages the metals have been classified according to the most common usage into six classes or groups. The reason for this system will appear after we have made a careful study of the metals and are ready to consider them in their relations to one another.

A few definitions will help us in our study of the text.

1. A Precipitate. Is any substance which having been dissolved in a liquid, falls to the bottom of the containing vessel on the addition of some chemical agent which decomposes the compound in solution.

2. A Reagent, Is any substance used to cause a chemical change in another substance for the purpose of identifying its component parts.

3. Filtration. Is the process of separating a precipitate from the liquid in which it is held by pouring the liquid and precipitate on some material such as filter paper which will retain the solid matter and allow the liquid to pass through.

4. Decantation. Is the process of separating a liquid from a precipitate by pouring off the liquid after the precipitate has been allowed to settle.

5. Analysis. Is the process of separating a compound into its component parts and determining the nature of each part.

6. Qualitative Analysis. Concerns itself with determining the nature of the component parts of a substance.

7. Quantitative Analysis. Determines the numerical relations between the component parts of substance, i. e., determines its percentage composition.

LEAD.

Symbol Pb. Atomic weight, 206.9.

The symbol is derived from the Latin name of lead (plumbum).

Lead rarely occurs free in nature. It is usually in the form of an oxid such as PbO or Pb_3O_4, as sulfid PbS (galena), carbonate $PbCO_3$ (cerussite), sulfate $PbSO_4$ (anglesite), etc.

Lead has been known since very early times, being mentioned in the books of Job and Numbers of the Old Testament.

Preparation. Lead is usually made from its ores by roasting them in furnaces of special design with some reducing agent such as carbon.

Exp. 1. Examine as many of the ores of lead as can be obtained. Note particularly:

a. The color.
b. The form.
c. The hardness.
d. The malleability.

These are the chief metallic characteristics which we should notice in all the metals studied.

Exp. 2. Heat a sample of lead on charcoal with a blow-pipe. Use the oxidizing flame. To obtain the oxidizing and reducing flames see the subject of Blow-pipe Analysis.

Note the color of the incrustation (the deposit on the charcoal.) Note the bead formed. Examine as to its metallic characteristics.

NOTE—For complete blow-pipe reactions of the metals see Blow-pipe Analysis.

Exp. 3. Solubility of lead.

Treat a small sample of the metal with:

a. Water, cold and hot.
b. Hydrochloric acid, cold and hot.
c. Nitric acid, cold and hot.

Reaction. $3Pb+8HNO_3=3Pb(NO_3)_2$ (lead nitrate) $+2NO+4H_2O$.

d. Concentrated sulfuric acid, hot and cold.

Reaction. $Pb+H_2SO_4=PbSO_4+2H_2O+SO_2$.

What is the best solvent for lead of those tested?

Note—Before testing a solution of a metal made by dissolving it in an acid it must be first freed from an excess of acid by evaporating nearly to dryness. The solution may then be diluted with water to make a quantity large enough to work with.

Exp. 4. With the solution which you have made or with one furnished by the instructor try the following reactions. Use small quantities of solution and reagents. One cc. of solution is enough.

1. Sodium hydroxid will precipitate white $Pb(OH)_2$.

With a solution of lead nitrate the reaction will be as follows:

$Pb(NO_3)_2 + 2NaOH = Pb(OH)_2 + 2NaNO_3$.

The lead hydroxid dissolves in an excess of the sodium hydroxid forming sodium plumbite Na_2PbO_2.

$Pb(OH)_2 + 2NaOH = Na_2PbO_2 + 2H_2O$.

2. Ammonium hydroxid precipitates the same but the precipitate is insoluble in excess.

$Pb(NO_3)_2 + 2NH_4OH = Pb(OH)_2 + 2NH_4NO_3$.

3. Sodium or ammonium carbonates precipitate white $PbCO_3$.

$Pb(NO_3)_2 + Na_2CO_3 = PbCO_3 + 2NaNO_3$. This reaction takes place if the solution is cold. If hot a compound is formed known as white lead.

$3Pb(NO_3)_2 + 3Na_2CO_3 + H_2O = Pb_3(OH)_2(CO_3)_2 + 6NaNO_3 + CO_2$.

4. Hydrogen or ammonium sulfid will pre-

cipitate black PbS.

$Pb(NO_3)_2+H_2S=PbS+HNO_3$. This precipitate is insoluble in cold dilute acids but soluble in hot nitric as follows:

Dilute nitric. $3PbS+8HNO_3=3Pb(NO_3)_2+4H_2O+2NO+3S$.

Concentrated acid. $3Pb(NO_3)_2+8HNO_3=3PbSO_4+4H_2O+8NO$.

5. Potassium iodid precipitates yellow PbI_2.

$Pb(NO_3)_2+2KI=PbI_2+2KNO_3$.

This precipitate is soluble in warm water from which solution it will crystallize in yellow scales on cooling. Add about four volumes of water and boil. Allow to cool slowly.

6. Potassium chromate precipitates yellow $PbCrO_4$.

$Pb(NO_3)_2+K_2CrO_4=PbCrO_4+2KNO_3$.

7. Potassium ferrocyanid precipitates white $Pb_2Fe(CN)_6$.

$2Pb(NO_3)_2+K_4FeCN_6=Pb_2Fe(CN)_6+4KNO_3$.

8. Hydrochloric acid or any soluble chlorid will precipitate white $PbCl_2$.

$Pb(NO_3)_2+2HCl=PbCl_2+2HNO_3$.

9. Sulfuric acid or soluble sulfates will precipitate white $PbSO_4$.

$Pb(NO_3)_2+H_2SO_4=PbSO_4+2HNO_3$.

10. Metallic zinc will completely precipitate lead in the metallic form from its solutions.

$Pb(NO_3)_2+Zn=Pb+Zn(NO_3)_2$.

NOTE—The reactions have been given under the subject of lead as a guide to the student. In general all reactions except those that are very difficult will be omitted. The student should be required to write them for himself, referring to the larger works on general chemistry and qualitative analysis for information.

Lead will react with many more reagents than are here stated but these given are most commonly used in analysis. For complete reactions see the larger works on qualitative analysis, such as Prescott and Johnson's Qualitative Analysis, etc.

SILVER.

Symbol Ag. Atomic weight, 108.93.

The name comes from the Latin name Argentum.

Silver occurs both in the free and combined state. Some of the most important ores are Ag_2S (argentite), Ag_3SbS_3 (pyrargyrite), AgCl (chlorargyrite), etc.

Silver has been known since very early times. It is one of the metals which is found in the earth in a pure state and all such were known long before those which need much manipulation to free them from their ores.

Exp. 5. Heat a sample of any good silver ore on charcoal with the oxidizing flame. The reduction of a silver ore is very difficult as the melting point of the metal is very high, 960° C. The student will be obliged to heat the ore a long time and will obtain a very small bead. Examine this for its metallic characteristics.

When pure, silver gives only a very slight incrustation but certain of its ores give one which is red.

Exp. 6. Solubility.

a. Try water, cold and hot.

b. Try dilute HNO_3 cold and hot.

c. Try concentrated HNO_3.

d. Try concentrated HCl.

e. Try concentrated H_2SO_4. Which is the best solvent? Write out all the reactions, following the models given for lead.

Exp. 7. With a solution of silver nitrate try the reactions of the following reagents:

1. Sodium hydroxid precipitates brown Ag_2O. Insoluble in excess but soluble in NH_4OH.

2. Ammonium hydroxid precipitates the same, soluble in excess.

The precipitate is so soluble that the ammonia must be very dilute. To a few drops of ammonia in a test tube add twenty times as much water, then add a few drops of this to the silver solution.

3. Sodium carbonate precipitates very light yellow Ag_2CO_3. Insoluble in excess but soluble in ammonium hydroxid.

4. Soluble sulfids such as H_2S precipitate black Ag_2S. Soluble in HNO_3. Insoluble in NH_4OH.

5. Potassium iodid precipitates light yellow AgI.

6. Potassium chromate precipitates red brown Ag_2CrO_4. Soluble in HNO_3 and in NH_4OH.

7. Hydrochloric acid and soluble chlorids precipitate white AgCl. Soluble in NH_4OH and KCN. With NH_4OH it forms $(NH_3)_3(AgCl)_2$. From this solution the AgCl is again precipitated on addition of HNO_3.

8. Potassium cyanid precipitates white AgCN. Soluble in excess to form AgCN(KCN). From this AgCN is precipitated with HNO_3.

MERCURY.

Symbol Hg. Atomic weight, 200.3.

The symbol comes from the Latin name hydrargyrum.

Mercury occurs in two modifications, as a monovalent and as a divalent element. It forms two classes of compounds which differ from each other greatly. These classes are designated as mercurous and mercuric compounds respectively.

Mercury occurs in the free state as well as in the form of ores. The most common of these is the sulfid HgS cinnabar. The others are for the most part amalgams of the other metals for which mercury has a great affinity.

Mercury was first mentioned about 300 B. C. in the writings of the Greek philosopher, Theophrastus.

Exp. 8. Examine a piece of cinnabar. Note the color, etc. Powder and note color again. Heat on charcoal. Heat in a small glass tube with a bit of charcoal. Note the deposit of metallic mercury on the walls of the tube.

Exp. 9. Try the solubility of both metallic mercury and cinnabar in the common acids. Try with a mixture of nitric and hydrochloric acids. How does the solubility of the mercury differ from the cinnabar?

Reaction for the mixture of nitric and hydrochloric acids:

$$3HCl+HNO_3= \left\{ \begin{array}{l} NOCl_2+Cl \\ NOCl+2Cl \end{array} \right\} +2H_2O, \text{ or}$$

This mixture is called "aqua regia" because it will dissolve all metals, among them gold, "the king of metals."

Exp. 10. Reactions for mercurous mercury Hg'.

Use a solution of mercurous nitrate $HgNO_3$.

1. Sodium hydroxid precipitates black Hg_2O. Insoluble in excess of the reagent. On boiling it decomposes into HgO and Hg.

2. Ammonium hydroxid or ammonium carbonate precipitates black amido mercurous nitrate ($Hg_2NH_2NO_3$.)

$2HgNO_3+2NH_4OH=NH_2Hg_2NO_3 + NH_4NO_3+ 2H_2O$.

3. Sodium carbonate precipitates first black Hg_2CO_3 which changes to a compound of variable composition,

4. H_2S produces black HgS mixed with Hg.

$2HgNO_3 + H_2S = HgS + Hg + 2HNO_3$.

This precipitate is soluble in aqua regia. By boiling with nitric acid it is changed to a white compound $HgNO_3 2HgS$.

5. Potassium iodid precipitates yellow green HgI. This dissolves in an excess of the reagent to to form $HgI_2 2KI$ while metallic mercury is precipitated.

$2HgI + 2KI = HgI_2(KI)_2 + Hg$.

6. HCl precipitates white HgCl. The same result is produced by any soluble chlorid. This precipitate is changed to black amido mercurous chlorid NH_2Hg_2Cl on adding ammonia.

7. H_2SO_4 and soluble sulfates precipitate white $HgSO_4$. This is slightly soluble in water so the precipitation is not complete.

8. Stannous chlorid in small quantities precipitates white HgCl and in excess reduces the HgCl to metallic mercury. So the precipitate will be first white then black.

9. Metallic copper or zinc precipitates metallic mercury from the solutions that have been acidified with HCl.

Reactions of mercuric compounds. Hg''.

Exp. 11. Use a solution of $HgCl_2$.

1. NaOH precipitates yellow HgO. Insoluble in excess.

2. NH_4OH or $(NH_4)_2CO_3$ precipitates white amido mercuric chlorid NH_2HgCl.

3. H_2S precipitates at first white $HgCl_2HgS_2$. This changes to a yellow compound, then to orange and at last to black HgS.

4. KI precipitates red HgI_2. Soluble in excess of the reagent to form $HgI_2(KI)_2$.

5. Stannous chlorid and other reducing agents produce first HgCl and then metallic mercury.

Make out a table of reactions comparing mercurous and mercuric mercury.

It will be noticed that the three metals lead, mercurous mercury and silver all form a white precipitate with HCl. We will see later that they are the only metals which give insoluble compounds with this acid. They are classed in a group by themselves called the first group.

A reagent which like HCl will precipitate the metals of a group is called a group reagent.

BISMUTH.

Symbol Bi. Atomic weight, 208.5.

Bismuth is a comparatively rare metal. It is found chiefly in the free state and in the form of Bi_2O_3 (bismuth ochre). Less frequently it is found as Bi_2S_3 (bismuthite), etc.

Exp. 12. Fuse a small sample of bismuth on charcoal. Note the character of the incrustation and the bead. How does it compare with that of lead in its physical properties?

Exp. 13. Try the solubility of bismuth in the common acids.

Exp. 14. Reactions.

Use a solution of $Bi(NO_3)_2$.

1. Pour a little of the bismuth solution into a test tube of water. A white precipitate of $Bi(OH)_2NO_3$ will be formed if there is not too much free acid present. Bismuth requires some free acid to keep it in solution and this will interfere with the test given. Add NH_4OH to a bismuth solution until a precipitate just begins to form, then a drop or two of acid so the precipitate just dissolves, then the solution will be in condition for the test.

$$Bi(NO_3)_2+2H_2O=Bi(OH)_2NO_3+2HNO_3.$$

2. NaOH or NH_4OH precipitates white $Bi(OH)_3$.

3. Na_2CO_3 or $(NH_4)_2CO_3$ precipitates white bismuth carbonate $(BiO)_2CO_3$.

4. Soluble sulfids precipitate Bi_2S_3. Soluble in HNO_3 but insoluble in $(NH_4)_2S$.

5. Acid sodium phosphate Na_2HPO_4 precipitates white $BiPO_4$.

6. KI precipitates BiI_3. Soluble in excess.

7. K_2CrO_4 precipitates a chromate of peculiar composition $[(BiO)_2CrO_4]_2Bi_2O_3$.

Reaction $8Bi(NO_3)_3+2K_2CrO_4+10H_2O=[(BiO)_2CrO_4]_2Bi_2O_3+4KNO_3+20HNO_3$. The precipitate is yellow.

8. To a small quantity of $SnCl_2$ add NaOH until the precipitate which forms at first is again dissolved, then to this solution add a little $Bi(NO_3)_3$.

White $Bi(OH)_3$ will be formed which will change to black Bi_2O_2 especially on heating.

$SnCl_2+2NaOH=Sn(OH)_2+2NaCl$.

$Sn(OH)_2+2NaOH=Na_2SnO_2$(sodium stannate) $+H_2O$.

$Bi(NO_3)_3+Na_2SnO_2$(sodium stannate)$=Na_2SnO_3+Bi_2O_2+3H_2O$.

COPPER.

Symbol Cu. Atomic weight, 63.6.

The symbol is derived from the Latin name *cuprum.*

Of all the metals copper is propably the first which was used very much. It occurs in the free state and needs little preparation to make it suitable for weapons and utensils.

It occurs free and in many compounds as CuO (tenorite or melaconite), Cu_2O (cuprite), $CuCO_3+Cu(OH)_2$ (malechite), etc.

Exp. 15. Mix a sample of a copper compound with Na_2CO_3 and heat on charcoal. Note the character of the metallic bead. There will be no incrustation.

Bend a loop in a platinum wire, heat and dip into borax. Heat the bead thus formed until it becomes clear then dip into a copper compound and heat again until clear. Note the color of the bead.

Exp. 16. Solution. Try to dissolve copper in all the common acids and note the gases given off. Write the reactions in each case. Examine all the different copper compounds you can find in the laboratory. Note the prevailing color.

Exp. 17. Reactions. Any copper solution may be used.

1. NaOH precipitates blue $Cu(OH)_2$. Insoluble in excess of reagent but soluble in NH_4OH. If an excess of the reagent is added and the solution boiled the blue $Cu(OH)_2$ becomes black $Cu(OH)_2CuO_2$.

2. NH_4OH precipitates a light blue copper compound which dissolves easily in excess producing a deep blue solution of copper ammonium sulfate $CuSO_4(NH_3)_4H_2O$.

Reaction. $CuSO_4+4NH_4OH=CuSO_4(NH_3)_4H_2O$.

If KCN is added to the solution the blue color will disappear with formation of $Cu(CN)_2(KCN)_2$.

3. Carbonates precipitate blue $Cu_2(OH)_2CO_3$.

4. Sulfids precipitate black CuS. Soluble in KCN and in HNO_3.

5. KCN precipitates yellow green $Cu(CN)_2$. Soluble in excess to form $Cu(CN)_2(KCN)_2$.

6. KI precipitates white Cu_2I_2 and free iodin. Because of the free iodin the precipitate is brown. Adding H_2SO_3 makes the precipitate white as this reagent removes the iodin.

7. $K_4Fe(CN)_6$ precipitates red brown $Cu_2Fe(CN)_6$.

8. Place a piece of clean iron wire in a copper solution. The copper will be precipitated on the wire.

CADMIUM.

Symbol Cd. Atomic weight, 112.4.

Cadmium is a rare metal occuring as carbonate and oxid with certain zinc ores. As the sulfid CdS it occurs in the mineral greenockite.

Exp. 18. Examine a piece of cadmium noting its physical properties.

Mix a compound of cadmium with sodium carbonate and heat on charcoal. Note the bead and the incrustation.

Exp. 19. Try the solubility of cadmium in the common acids.

Exp. 20. With a solution try the following reagents:

1. NaOH precipitates white $Cd(OH)_2$ Insoluble in excess.
2. NH_4OH precipitates the same compound, soluble in excess.
3. Na_2CO_3 and $(NH_4)_2CO_3$ precipitate white $CdCO_3$.
4. H_2S precipitates yellow CdS. Insoluble in $(NH_4)_2S$. Soluble in warm dilute acid.
5. KCN precipitates white $Cd(CN)_2$. Soluble in excess to form $Cd(CN)_2(KCN)_2$.
6. K_2CrO_4 precipitates slowly a yellow chro-

mate having this composition, $Cd_2(OH)_2CrO_4$.

Reaction. $2Cd(NO_3)+K_2CrO_4+2H_2O=Cd_2(OH)_2CrO_4+2KNO_3+2HNO_3$.

ARSENIC.

Symbol As. Atomic weight, 75.

Arsenic although a non-metal of the nitrogen family exhibits so many metallic properties that it must be classed with the metals for purposes of analysis. For properties and general reactions see Part 1.

Exp. 21. Dissolve a small quantity of As_2O_3 in hydrochloric acid and try the following reactions:

1. H_2S produces a yellow precipitate of As_2S_3. Treat the precipitate with the following solvents:

a. HCl, b. NH_4OH, c. $(NH_4)_2CO_3$, d. $(NH_4)_2S_x$. With the latter $(NH_4)_3AsS_4$ is produced which will give As_2S_5 on treatment with HCl.

$(NH_4)_2S_x$ or yellow ammonium sulfid is the best solvent of As_2S_3. The x indicates that the exact quantity of sulfur in the compound is unknown.

Arsenic solutions give no other solutions with the common reagents.

NOTE—Arsenic exists both as a tri and a pentavalent element. If a pentavalent compound is treated with H_2S it is first reduced to the trivalent compound and then the arsenic is precipitated as As_2S_3. The reduction takes place more quickly if the solution is warm.

ANTIMONY.

Symbol Sb. Atomic weight, 120.

The symbol comes from the Latin name, *stibium.*

Antimony has been known since Old Testament times although not in the metallic form. The sulfid Sb_2S_3 was the first compound well known.

Antimony occurs in the free state and in many compounds, of which Sb_2S_3 (stibnite) is the most common. It does not occur in great quantities.

Exp. 22. Examine a piece of antimony. Heat a piece on charcoal and note the incrustation. On this drop a little $Co(NO_3)_2$ solution and heat again. Note change in color of the incrustation. See Blow-Pipe Analysis. Note the hardness, malleability, etc., of the bead.

Exp. 23. Try the solubility of antimony in the common acids. Try in a mixture of HNO_3 and HCl. What is the best solvent?

Exp. 24. With a solution of $SbCl_3$ try the following:

1. Water precipitates white SbOCl (antimony oxychlorid).

$SbCl_3+H_2O=SbOCl+2HCl$. If too much free acid is present the reaction will not take place. See Bismuth, Exp. 14, 1.

2. NaOH precipitates white SbOOH. Soluble in excess to form $NaSbO_2$.

3. NH_4OH or $(NH_4)_2CO_3$ precipitate the same. Insoluble in excess.

4. H_2S precipitates red Sb_2S_3. Insoluble in $(NH_4)_2CO_3$ but soluble in $(NH_4)_2S_x$.

$Sb_2S_3+(NH_4)_2S_x=(NH_4)_3SbS_4$. From this solution HCl precipitates Sb_2S_5.

$2(NH_4)_3SbS_4 + 6HCl = Sb_2S_5+6NH_4Cl+3H_2S$.

5. Place a drop of antimony solution on a piece of platinum foil and touch it with a piece of zinc. The antimony will be precipitated on the foil as a black stain.

TIN.

Symbol Sn. Atomic weight, 118.5.

The symbol comes from the Latin name of tin, *stannum.*

Tin, like arsenic, mercury and many other elements, forms compounds in which the element acts in two valence relations. Tin acts as a bi- and a tetravalent element forming stannous and stannic compounds.

Tin was one of the metals recognized very early in the world's history. It is found in the free state and also in the form of compounds. The chief ore of tin is the oxid (SnO_2) tin stone or cassiterite.

Exp. 24. Examine a piece of tin. Bend it and note the crackling noise. Fuse a small piece on charcoal. Does it fuse easily? Is there an incrustation?

Exp. 25. Try to dissolve tin in the common acids both dilute and concentrated. The reactions are different especially in the case of the nitric acid which forms two compounds, as follows:

Dilute. $4Sn+10HNO_3=4Sn(NO_3)_2+NH_4NO_3+3H_2O$.

Concentrated. $3Sn+4HNO_3=3H_2SnO_3$ (stannic acid)$+4NO+H_2O$.

Reactions for stannous tin Sn''.

Exp. 26. With a solution of $SnCl_2$ try the following:

1. NaOH precipitates white $Sn(OH)_2$ soluble in excess to form Na_2SnO_2 (sodium stannite).

2. NH_4OH or $(NH_4)_2CO_3$ precipitate the same, soluble in excess.

3. H_2S precipitates black or dark brown SnS. Soluble in $(NH_4)_2S_x$ forming ammonium thio-stannite $(NH_4)_2SnS_3$.

From this solution HCl precipitates yellow SnS_2.

4. Stannous compounds are strong reducing agents. Treat a solution of silver nitrate with $SnCl_2$. Metallic silver will be formed. Try the same with $HgCl_2$. A white precipitate of HgCl is formed which will change to black Hg especially on heating.

Reactions for stannic tin. Sn''''.

On standing, stannic solutions decompose with formation of $Sn(OH)_2$.

Exp. 27. To change a stannous solution to a stannic. Heat a solution of stannous chlorid with HCl and a few crystals of $KClO_3$. Chlorin will be set free which will oxidize the stannous chlorid to stannic $SnCl_4$. Boil the solution until the odor of chlorin disappears and with it try the following:

1. NaOH precipitates white stannic acid H_2SnO_3. Soluble in excess to form sodium stannate Na_2SnO_3.
2. NH_4OH precipitates the same, insoluble in excess.
3. H_2S precipitates yellow SnS_2. Soluble in $(NH_4)S_x$ to form ammonium thio-stannate $(NH_4)_3SnS_3$.

ALUMINUM.

Symbol Al. Atomic weight, 27.1.

The compounds of aluminum, the alums and alumina (Al_2O_2), have been known for a long time but it was not until 1827 that the free metal was made. It was first obtained by the chemist Wœhler. Since the introduction of the electric furnace the metal has become common and comparatively cheap.

Except silicon and oxygen, aluminum is the most widely distributed element. It occurs in many forms, as Al_2O_3 in the mineral corundum. In combination with potassium and sodium it forms the great classes of minerals, the micas, feldspars and the products resulting from their decomposition, the clays.

Exp. 28. Examine as large a piece of aluminum as can be found. What is its most striking characteristic? Fuse a small sample on charcoal. Examine the bead with respect to its physical properties and compare with tin. Heat a bit of Al_2O_3 on charcoal, add $Co(NO_3)_2$ and heat again. Note color.

Exp. 29. Try the solubility of Al in acids. Try NaOH and KOH. Write the reactions. With a solution try the following:

1. NaOH precipitates white $Al(OH)_3$. Soluble in excess to form $NaAlO_2$ (sodium aluminate).

2. Ammonium hydroxid precipitates the same, insoluble in excess in the presence of NH_4Cl.

3. Na_2CO_3 and $(NH_4)_2CO_3$ precipitate the same with evolution of CO_2.

$$2AlCl_3+3(NH_4)_2CO_3+3H_2O = 2Al(OH)_3+6NH_4Cl+3CO_2.$$

4. $(NH_4)_2S$ precipitates the same with evolution of H_2S.

$$2AlCl_3+3(NH_4)_2S+3H_2O = 2Al(OH)_3+6NH_4Cl+3H_2S.$$

5. Na_2HPO_4 precipitates white $AlPO_4$.

NOTE —Non-volatile substances of organic origin such as sugar, tartaric acid, etc., prevent precipitations 1, 2, 3 and 4.

CHROMIUM.

Symbol Cr. Atomic weight, 52.1.

Chromium is not a very common substance

and does not occur in the free state. The chief sources of the metal are $PbCrO_4$ (lead chromate) and $Fe_2Cr_2O_4$ (chrome iron stone or chromite).

Chromium is made from its compounds by reducing them with some powerful reducing agent such as metallic magnesium or sodium, or by means of the electric furnace. It is a tin white metal somewhat harder than glass and melts at a very high temperature, higher than the melting point of platinum. The pure metal dissolves in the common acids.

Exp. 30. Make a borax bead and dip it into a solution of some chromium compound. Heat in the flame of a burner. Note the color. With a solution try the following reactions:

1. $NaOH$ precipitates gray green $Cr(OH)_3$. Soluble in excess to form a dark green solution of sodium chromite $NaCrO_4$.

2. NH_4OH precipitates the same. Insoluble in excess except in slight degree and not at all if NH_4Cl is present.

3. Na_2CO_3 and $(NH_4)_2CO_3$ precipitate $Cr(OH)_3$ liberating CO_2. See Al 3.

4. $(NH_4)_2S$ precipitates the same with evolution of H_2S.

5. Na_2HPO_4 precipitates gray green $CrPO_4$. Soluble in acids and $NaOH$.

6. Heat a salt of chromium such as $Cr(OH)_3$ on platinum foil with a mixture of KNO_3 and Na_2-

CO_3. A green chromate will be formed. Confirm by dissolving in hot water, adding acetic acid to decompose the Na_2CO_3, then adding lead acetate. A yellow precipitate of lead chromate will be formed.

$2Cr(OH)_3+3KNO_3+2Na_2CO_3=2Na_2CrO_4+3KNO_2+3H_2O+2CO_2$.

IRON.

Symbol Fe. Atomic weight, 56.

The name comes from the Latin name *ferrum.*

Iron exists in two states of valence, i. e., of 2 and 3. It is the most useful of all metals and one of the most common. It has been known for a long time although probably not as long as those metals which occur more frequently in the free state. It was first made from its ores by the ancient Hindus.

Iron rarely occurs in the free state because it has such a great affinity for oxygen. The most common ores are the oxids, Fe_2O_3 (red haematite), $H_6Fe_4O_9$ (brown hematite), Fe_3O_4 (magnetic iron ore), $FeCO_3$, FeS_2, etc.

Exp. 31. Examine a piece of pure iron such as piano wire. Fuse on charcoal. Test the bead thus made with a magnet. Heat a bit of iron or one of its compounds in a borax bead. Note the color when hot and when cold.

Exp. 32. Make a solution of $FeCl_2$ and test in the following manner.

1. NaOH precipitates $Fe(OH)_2$. This changes to a dirty green, then to brown by oxidation to $Fe(OH)_3$. The precipitation is not complete if ammonium salts are present.

2. NH_4OH partially precipitates $Fe(OH)_2$.

3. Na_2CO_3 and $(NH_4)_2CO_3$ precipitate white $FeCO_3$ which quickly changes to $Fe(OH)_3$.

4. H_2S gives no precipitate when the solution is acid. When neutral it precipitates the iron as FeS.

5. $(NH_4)_2S$ precipitates black FeS.

6. KCN precipitates brown $Fe(CN)_2$. Soluble in excess to form $K_4Fe(CN)_6$, potassium ferrocyanid.

7. KSCN (potassium sulfocyanid) has no effect on a ferrous solution if free from ferric.

8. $K_4Fe(CN)_6$ (potassium ferro-cyanid) precipitates light blue potassium ferrous-ferro-cyanid, $K_2Fe_3[Fe(CN)_6]_2$.

9. $K_3Fe(CN)_6$ (potassium ferri-cyanid) precipitates a deep blue compound called "Turnbull's blue," $Fe_3[Fe(CN)_6]_2$.

Exp. 33. With a ferric solution such as ferric nitrate try the following:

1. NaOH and NH_4OH precipitate red brown $Fe(OH)_3$.

2. Na_2CO_3 and $(NH_4)_2CO_3$ precipitate the same with evolution of CO_2.

3. H_2S reduces ferric salts to ferrous with precipitation of sulfur.

4. $(NH_4)_2S$ reduces ferric iron to ferrous, precipitates sulfur and FeS.

5. Na_2HPO_4 precipitates yellowish white $FePO_4$.

6. KSCN produces a blood red color in a ferric solution due to formation of $Fe(SCN)_3$. This is one of the most delicate reactions for ferric iron and is the one most used to distinguish between ferrous and ferric compounds.

7. $K_4Fe(CN)_6$ precipitates "Prussian blue," $Fe_4[Fe(CN)_6]_3$.

8. $SnCl_2$ and other reducing agents reduce the ferric compounds to ferrous.

NOTE—The ferrous salts change to ferric on being exposed to the air. Thus nearly all solutions of ferrous salts will give reactions for ferric. If it is desired to change a ferrous compound completely to a ferric, add HNO_3 and boil or add HCl and $KClO_3$.

Reaction.

$$6FeCl_2+KClO_3+6HCl=KCl+3H_2O+6FeCl_3.$$

On the other hand if it is desired to change a ferric solution to a ferrous reduce it with a reducing agent such as $SnCl_2$.

$$2FeCl_2+SnCl_2=2FeCl_2+SnCl_4.$$

Make out a table comparing the reactions of ferrous and ferric iron.

NICKEL.

Symbol Ni. Atomic weight, 58.4.

Nickel ore was first known about 1694 and was called Kupfer-nickel or false copper as it had much the appearance of copper. Many attempts were made to prepare copper from it but without result. In 1754 the first pure nickel was made.

Nickel occurs in many different ores although not in great quantity. It is usually found in company with cobalt, a metal which is much like it in many particulars. The most common ores of nickel are NiAs (nickeline or Kupfer-nickel), NiAsS (nickel glance), etc.

Exp. 34. Examine a sample of nickel. Note the metallic characteristics. Examine as many salts of nickel as can be found. What is the characteristic color? Fuse a sample of the metal on charcoal. Test the bead with a magnet. Test with a borax bead.

Exp. 35. Try the solubility of nickel in the common acids. With one of the solutions thus made try the following reactions:

1. NaOH precipitates apple-green $Ni(OH)_2$, insoluble in excess. Soluble in NH_4Cl. To this precipitate add an excess of NaOH and boil, then add bromin water. The apple-green $Ni(OH)_2$ will be oxidized to black $Ni(OH)_3$.

2. NH_4OH precipitates the same, soluble in excess, forming a blue solution. This precipitation is prevented by ammonium salts.

3. Na_2CO_3 and $(NH_4)_2CO_3$ produce apple-green carbonates of varying composition.

4. H_2S produces no precipitate in a nickel solution containing free acid. In a neutral solution the Ni is partially precipitated as NiS. Acetic

acid is an exception, as the Ni is completely precipitated from a solution of nickel acetate.

5. $(NH_4)_2S$ precipitates NiS.

6. Na_2HPO_4 precipitates apple-green $Ni_3(PO_4)_2$

7. KCN precipitates yellow green $Ni(CN)_2$, soluble in excess to form $Ni(CN)_2(KCN)_2$. The $Ni(CN)_2$ will be again precipitated from this solution on addition of HCl.

To a solution of $Ni(CN)_2(KCN)_2$ add an excess of NaOH and boil, then add bromin water and $Ni(OH)_3$ will be formed.

8. $K_4Fe(CN)_6$ precipitates green $Ni_2Fe(CN)_6$.

9. $K_3Fe(CN)_6$ precipitates yellow-brown $Ni_3Fe(CN_6)_2$.

COBALT.

Symbol Co. Atomic weight, 59.

Cobalt very much resembles nickel in its properties. The two metals usually occur together and are only separated with great difficulty. The metal was first recognized in 1742.

Cobalt compounds were known long before the metal itself was isolated. Its compounds were used for coloring glass.

Exp. 36. Cobalt acts in much the same way as nickel when heated on charcoal. Try a sample of metallic cobalt or one of its salts in a borax bead.

Exp. 37. The solubility of cobalt is about the same as that of Ni, but the reactions are quite different. Note the color of as many cobalt salts as can be obtained. Then with a solution try the following reactions.

1. NaOH precipitates a blue salt of doubtful composition. If an excess of the reagent is added and then boiled $Co(OH)_2$ will be formed. On standing the red $Co(OH)_2$ will gradually oxidize to brown $Co(OH)_3$. Bromin water gives a reaction similar to that under Ni, 1.

2. NH_4OH precipitates a blue compound from a neutral solution. This precipitate does not appear in a solution containing ammonium salts.

3. Na_2CO_3 and $(NH_4)_2CO_3$ precipitate a red-lilac carbonate of doubtful composition.

4. H_2S precipitates CoS from solutions which do not contain free mineral acid.

5. $(NH_4)_2S$ precipitates the same.

6. Na_2HPO_4 precipitates blue $Co_3(PO_4)_2$.

7. KCN precipitates red-brown $Co(CN)_2$. Soluble in excess of the reagent to form $Co(CN)_2$-$(KCN)_2$ or $K_4Co(CN)_6$. If NaOH and bromin water are added to this solution there is no precipitate. See Ni, 7.

8. $K_4Fe(CN)_6$ precipitates blue-green Co_2Fe-$(CN)_6$.

9. $K_3Fe(CN)_6$ precipitates brown $Co_3Fe(CN_6)_2$.

10. KNO_2 added in excess to a solution of cobalt to which acetic acid has been added precipi-

tates yellow $Co(CN_2)_3(KNO_2)_3$. The precipitate forms slowly, especially in dilute solutions.

Reaction. $Co(NO_3)_2+7KNO+2HC_2H_3O_2=Co(NO_2)_3(KNO_2)_3+2KNO_3+2KC_2H_3O_2+H_2O+NO$.

MANGANESE.

Symbol Mn. Atomic weight, 55.

The ore of manganese, pyrolusite (MnO_2), has been known for a long time, being first mentioned by Pliny. He tells us that the ore was used to remove impurities from glass. In early days no distinction was made between pyrolusite and the magnetic oxid of iron. It was believed that both were iron oxids. In 1774 the metal manganese was discovered.

Manganese occurs chiefly in the mineral pyrolusite, also in braunite (Mn_2O_3), hausmannite (Mn_2O_4), etc.

Manganese occurs in four forms of valence, 2, 3, 6 and 7. In the first two forms it acts as a metallic substance, forming manganous and manganic compounds, while in the other two it acts as a nonmetal forming manganic and permanganic acids. These are not well known in the free state, but their salts are common; i. e., K_2MnO_4 (potassium manganate) and $KMnO_4$(potassium permanganate).

Properties.

Manganese is a grey or white metal which looks much like cast iron. When pure it has so great an affinity for oxygen that it cannot be exposed to the air, but must be kept under oil or in a sealed tube. Alloyed with iron it is more permanent. It is very easily soluble in acids.

Exp. 38. Heat a sample of manganese compound in a borax bead. Mix a sample with KNO_3 and Na_2CO_3 and heat on a platinum foil.

Reaction. $MnSO_4 + 2Na_2CO_3 + 3KNO_3 = Na_2MnO_4 + Na_2SO_4 + 2KNO_2 + 2CO_2$.

Exp. 39. With a solution try the following reactions:

1. $NaOH$ precipitates white $Mn(OH)_2$. This is not precipitated in the presence of NH_4Cl. On standing the $Mn(OH)_2$ will oxidize to brown $Mn(OH)_3$.

2. NH_4OH precipitates the same in a neutral solution. In a solution which contains ammonium salts the precipitate does not appear at first but, on standing, the manganese is completely precipitated as $Mn(OH)_3$.

3. Na_2CO_3 and $(NH_4)_2CO_3$ precipitate white $MnCO_3$.

4. H_2S gives no precipitate.

5. $(NH_4)_2S$ precipitates flesh-colored MnS.

6. Na_2HPO_4 precipitates white $Mn_3(PO_4)_2$.

7. $K_4Fe(CN)_6$ precipitates white $Mn_2Fe(CN)_6$.

8. $K_3Fe(CN)_6$ precipitates brown $Mn_3Fe(CN_6)_2$.

9. Place a little Pb_3O_4 in a test tube with

about 2 cc. concentrated HNO_3, then add a little manganese solution and warm. The solution will become red from formation of permanganic acid. If the color is obscured by a precipitate, filter.

Reaction. $2MnSO_4 + 5Pb_3O_4 + 26HNO_3 = 2HMnO_4 + 2PbSO_4 + 13Pb(NO_3)_2 + 12H_2O$.

ZINC.

Symbol Zn. Atomic weight, 65.4.

The alloy of zinc called brass was known to the ancients; but it was not until the last of the 18th century that the nature of the metal was fully understood.

Zinc occurs in a great many compounds, calamine ($ZnCO_3$), zinc blende (ZnS), franklinite $(ZnFe)O+(Fe_2O_3)$, etc.

Exp. 40. Examine a piece of zinc. Fuse on charcoal. Note the incrustation. Treat this incrustation with $Co(NO_3)_2$ and heat with the blow pipe. Note change in color.

Exp. 41. Try the solubility of the metal in acids and NaOH. With a solution try the following:

1. NaOH precipitates white $Zn(OH)_2$, soluble in excess forming Na_2ZnO_2 (sodium zincate).
2. NH_4OH precipitates the same, soluble in excess.
3. Na_2CO_3 precipitates white $Zn_2(OH)_2CO_3$.
4. $(NH_4)_2CO_3$ precipitates the same, soluble in

excess of the reagent.

5. H_2S gives no precipitate in solutions which contain a free mineral acid. In neutral or alkaline solutions it produces white ZnS.

6. $(NH_4)_2S$ precipitates the same.

7. Na_2HPO_4 precipitates white $Zn_3(PO_4)_2$.

8. KCN precipitates white $Zn(CN)_2$, soluble in excess, forming $Zn(CN)_2(KCN)_2$.

9. $K_4Fe(CN)_6$ precipitates white $Zn_2Fe(CN)_6$.

10. $K_3Fe(CN)_6$ precipitates yellow brown $Zn_3Fe(CN_6)_2$.

BARIUM.

Symbol Ba. Atomic weight, 137.4.

Barium is very difficult to obtain in the metallic state and has little importance except in the form of its compounds. It is a soft white metal which oxidizes easily when exposed to the air. In many of its properties it resembles closely the metals potassium and sodium.

Some of the reactions of barium are important.

Exp. 41. Fuse a salt of barium on charcoal and note the color of the residue. Add $Co(NO_3)_2$ and heat again. Test the residue with blue litmus paper after adding a little water.

Dip a platinum wire in a barium solution and heat in a colorless flame.

Exp. 42. With a solution of barium try the following:

1. NaOH precipitates white $Ba(OH)_2$ from concentrated solutions.

2. NH_4OH gives no precipitate.

3. Na_2CO_3 and $(NH_4)_2CO_3$ precipitate white $BaCO_3$, soluble to a small degree in water containing CO_2. The precipitation is complete in solutions containing NH_4OH in excess.

The precipitate forms an acid carbonate of barium in solutions containing CO_2, as follows:

$BaCO_3+CO_2+H_2O=BaH_2(CO_3)_2$.

4. Na_2HPO_4 precipitates a white acid phosphate $BaHPO_4$. In the presence of ammonia, $BaNH_4PO_4$ is formed instead.

5. K_2CrO_4 precipitates yellow $BaCrO_4$.

6. H_2SO_4 and soluble sulfates precipitate white $BaSO_4$.

Ammonium oxalate, $(NH_4)_2C_2O_4$, precipitates white BaC_2O_4 from concentrated solutions.

STRONTIUM.

Symbol Sr. Atomic weight, 87.6.

Strontium is very much like barium in its properties.

Exp. 43. Test a strontium compound on charcoal with cobalt nitrate and with the flame as you did barium.

Exp. 44. With a solution try the following:

1. NaOH precipitates white $Sr(OH)_2$. Somewhat soluble in water.

2. NH_4OH forms no precipitate.

3. Na_2CO_3 and $(NH_4)_2CO_3$ precipitate white $SrCO_3$.

4. Na_2HPO_4 precipitates white $SrHPO_4$.

5. K_2CrO_4 precipitates yellow $SrCrO_4$ from concentrated solutions. The precipitate will not appear at once if the solution is dilute. The addition of alcohol causes it to form faster.

6. H_2SO_4 precipitates white $SrSO_4$. This is somewhat soluble in water, so will not appear if the solution is very dilute.

7. $(NH_4)_2C_2O_4$ precipitates white SrC_2O_4.

CALCIUM.

Symbol Ca. Atomic weight, 40.

Of the three metals, barium, strontium and calcium, the last is by far the most important. In the metallic state it is of little importance as yet, but it is believed that it may be manufactured cheaply in the electric furnace and may become very useful as a substitute for potassium and sodium.

Calcium is very widely distributed in nature. It forms a large share of the earth's crust. In the form of carbonates it occurs in the important rocks, the limestones, chalks, etc. It occurs in the bones of animals in the form of phosphate and in many other compounds.

Exp. 45. Repeat Exp. 43 with a calcium

compound. Note the difference between the strontium and calcium flames.

Exp. 46. Try the following with a calcium solution.

1. NaOH precipitates white $Ca(OH)_2$. Somewhat soluble in water.

2. NH_4OH forms no precipitate.

3. Na_2CO_3 and $(NH_4)_2CO_3$ precipitate white $CaCO_3$. Soluble in water containing CO_2. See barium 3.

4. Na_2HPO_4 precipitates white $CaHPO_4$. In the presence of NH_4OH, $Ca_3(PO_4)_2$ is formed.

5. H_2SO_4 and soluble sulfates precipitate white $CaSO_4$. This is somewhat soluble in water. The precipitate is not formed in dilute solutions.

6. $(NH_4)_2C_2O_4$ precipitates white CaC_2O_4.

NOTE—The three metals, barium, strontium and calcium, have so many characteristics in common that they are classed together as the *alkaline earth metals*. They often occur together in nature.

MAGNESIUM.

Symbol Mg. Atomic weight, 24.36.

The salt of magnesium, $MgSO_4$ (Epsom salt), was first recognized in the waters of a mineral spring at Epsom, England. The metal itself was prepared by Davy at the beginning of the 19th century.

Exp. 47. Examine a bit of metallic magnesium. With a pair of tongs hold a piece in the flame of a burner. What is the residue formed? Heat some of this residue on charcoal with $Co(NO_3)_2$. Note the color. Try the same with any compound of magnesium. What uses can you name for magnesium? How does its importance compare with that of the metals of the alkaline earths?

Exp. 48. Try the solubility of magnesium, and with a solution try the following reagents:

1. $NaOH$ precipitates white $Mg(OH)_2$. This is soluble in NH_4Cl so that it does not form when ammonium salts are present.

2. NH_4OH precipitates the same incompletely, in a solution free from ammonium salts such as NH_4Cl.

3. $(NH_4)_2CO_3$ and Na_2CO_3 precipitate a white carbonate of doubtful composition. If the solution is hot at the time of precipitation $Mg_3(OH)_2(CO_3)_2$ is formed.

4. Na_2HPO_4 precipitates white $MgHPO_4$. On boiling this changes to $Mg_3(PO_4)_2$. In the presence of NH_4Cl, $MgNH_4PO_4$ is precipitated.

5. $(NH_4)_2C_2O_4$ gives a white precipitate of MgC_2O_4 in a concentrated solution.

THE ALKALI METALS.

The three metals, sodium, potassium and ammonium, are called the alkali metals, since they are the sources of the most common alkalies such as $NaOH$, KOH and NH_4OH. They form salts with all acids, and as these salts are nearly all soluble in water there are very few precipitates formed with the common reagents. For this reason we cannot apply the same methods in the detection of these three metals that we have in the preceding. Sodium and potassium are recognized by the color which they give to a flame and ammonium compounds by the odor of NH_3 which they will give when heated with a strong alkali such as KOH or NaOH.

AMMONIUM.

Formula NH_4. Molecular weight, 18.04.

Ammonium (NH_4) has never been isolated, but as it is well known in the form of its compounds and acts just like the other metals, chemists have come to consider it to be as real a metal as if it could be handled and its weight, metallic lustre, etc., determined.

Exp. 49. Any compound of ammonium can be used for the following tests as all are soluble in water.

1. Treat the solution with a little concentrated NaOH and heat. Note the odor of ammonia. Hold a glass rod which has been dipped in HCl over the mouth of the test tube. What are the white fumes?

2. "Nessler's test." Treat a solution of an ammonium compound with "Nessler's" reagent. Note the brown precipitate. This is Hg_2INH_2O. The reaction is best shown in dilute solutions.

Nesslers reagent is made by adding KI to a solution of $HgCl_2$ until the precipitate first formed is again dissolved. To this add a solution of KOH and filter. Keep in a well'stoppered bottle.

Reaction for the Nesslers test.

$HgI_2 + 2KI = HgI_2(KI)_2$.

$2HgI_2(KI)_2 + 4NH_4OH = Hg_2INH_2O + 3NH_4I + 4KI$.

POTASSIUM.

Symbol K. Atomic weight, 39.15.

The symbol of potassium comes from its Latin name, *kalium*.

Potassium is found chiefly in the form of a carbonate in wood ashes. From ashes it was prepared until a few years ago when a great deposit of potassium salts was discovered in northern Germany at a place called Stassfurt. In the form of a silicate it occurs in great quantities in the potash feldspars. Many other minerals contain the element but the chief commercial source is the Stassfurt deposit.

Exp. 50. Examine a piece of metallic potassium. Why is it kept under benzine? Throw a small piece into water. Write the reaction.

Exp. 51. Test a solution as follows:

1. Heat on a platinum wire. Mix with a sodium solution and test the two together in the flame. Look at the flame through a piece of blue glass. Effect?

2. $HNaC_4H_4O_6$ (acid sodium tartrate) precipitates white $HKC_4H_4O_6$ from a concentrated solution.

3. To a small quantity of sodium nitrite add a little acetic acid and cobalt nitrate solution. To this add a solution of a potassium salt, shake and allow to stand. After a time a yellow precipitate of $Co(NO_3)_2(KNO_2)_3$ will form. See Exp. 10, under cobalt.

SODIUM.

Symbol Na. Atomic weight, 23.05.

The symbol of sodium comes from its Latin name, *natrium*.

Sodium is widely distributed. In the form of its chlorid it is found in sea water, in the carbonate it is found in wood ashes and in mineral waters, as silicate it occurs in certain feldspars, as nitrate in Chilian saltpeter, etc.

Sodium, as well as potassium, was first prepared by Sir Humphrey Davy in 1807.

Exp. 51. Examine a piece of metallic sodium. Compare with potassium. Throw a small piece into water.

Test a solution of sodium on the platinum wire in a flame.

1. $K_2H_2Sb_2O_7$ (potassium pyroantimonate) precipitates white $Na_2H_2Sb_2O_7$ from neutral solutions of sodium.

All reactions of sodium are very unsatisfactory so that the flame test is the one most commonly used.

NOTE—It has been found most profitable at this part of the work to require the students to analyze a series of 25 or 50 unknown solutions to fix the preceding reactions firmly in mind. The student should be allowed to choose his own method of analysis and should be thrown as much as possible upon his own resources. After this preliminary work he is ready for a study of metal separation. It is often found advantageous to make out a table of reactions which will contain all the reactions in a small space, so that the worker can see at a glance what any metal will do with any reagent. The outline of such a table is suggested below.

A table for analysis of an unknown may be made out somewhat as follows. There is no particular order to be followed and this table is not at all complete. It is merely a suggestion.

	Pb	Ag	Hg	Cu	Bi	Cd	Hg''	Fe''	Fe'''	Cr	etc.
HCl	W	W	W	—	—	—	—	—	—	—	
H_2SO_4	W	—	W	—	—	—	—	—	—	—	
H_2S	Bl'k	B	B	B	B	Y	B	—	—	—	
NaOH	W	Br'n	B	Gr	W	W	Y	W	Br	Gr	
etc.											

In this way make out a scheme that will contain all the metals and all the reagents. Do not omit anything.

SEPARATIONS OF THE METALS.

It will be noticed in comparing the reactions that certain metals have similar reactions. For example, lead, silver and mercurous mercury all give a white precipitate with HCl; lead, mercurous mercury, barium, calcium and strontium give a white precipitate with H_2SO_4, etc. These common reactions may be gathered together and stated in a series of principles, as follows:

I. The nitrates, chlorates and acetates of all metals are soluble in water except in four cases, viz: Bismuth, tin, antimony and certain salts of mercury require some free acid to hold them in solution.

II. All oxids and hydroxids are insoluble in water except those of the alkali metals. The oxids and hydroxids of barium, strontium and calcium are slightly soluble. Hence the fixed alkaline hydroxids, NaOH and KOH, precipitate solutions of all other metals, barium, calcium and strontium incompletely.

II, a. The precipitate is a hydroxid except in the cases of silver and mercurous mercury when it is an oxid.

b. The precipitate redissolves in the case of eight metals, forming if NaOH is used Na_2PbO_2 (sodium plumbite), Na_2SnO_2 (sodium stannite), Na_2SnO_3 (sodium stannate), Na_2SbO_2 (sodium antimonite), Na_2SbO_3, Na_2ZnO_2, $NaAlO_2$ and $NaCrO_2$.

III. NH_4OH precipitates solutions of all the metals except Ba, Sr and Ca and the alkali metals

K and Na. Mn and Mg are precipitated incompletely and not at all in the presence of NH_4Cl.

a. In most cases the precipitate is a hydroxid. With silver it is an oxid and with both mercurous and mercuric mercury it is a compound of peculiar composition, depending on the nature of the mercury in solution.

b. The precipitate redissolves in six cases, i. e., Ag, Cu, Cd, Co, Ni and Zn.

IV. The chlorids of lead, silver and mercurous mercury are insoluble in water, therefore HCl and soluble chlorids will precipitate these three metals, lead incompletely.

V. The iodids of lead, mercury and copper are insoluble, hence HI and soluble iodids will precipitate these metals.

VI. The sulfates of lead, mercurous mercury, barium, calcium and strontium are insoluble, those of mercury and calcium slightly soluble. Hence H_2SO_4 and soluble sulfates precipitate these metals, mercury and calcium incompletely.

VII. The sulfids of all the metals are insoluble. The alkalies and the alkaline earth metals are not precipitated. Soluble sulfids such as H_2S will precipitate Pb, Ag, Hg, Cu, Cd, Bi, Sn, Sb and As, while an alkaline sulfid such as $(NH_4)_2S$ will precipitate Fe, Al, Cr, Zn, Mn, Co and Ni.

The result is a sulfid, except in the cases of Al and Cr when the precipitate is a hydroxid.

VIII. The carbonates of all the metals except the alkalies and As are insoluble, hence soluble carbonates such as those of the alkalies will precipitate all the metals from their solutions.

NOTE—As forms no carbonate.

CLASSIFICATION OF THE METALS FOR ANALYSIS.

Making use of the facts shown in the principles we may classify the metals into six groups. These groups are as follows:

I. Contains metals precipitated by HCl, Pb, Ag and Hg′. The precipitates are chlorids and with the exception of lead chlorid are insoluble in water. Lead chlorid is slightly soluble, so the metal will appear in the second as well as the first group.

The reagent which precipitates all the metals of a group is called a *group reagent.*

II. Precipitated by H_2S and not by HCl.

NOTE—The solution must be slightly acid.

Hg″, Pb (residue from group I), Bi, Cu, Cd, As, Sb and Sn.

The sulfids of As, Sb and Sn are soluble in yellow ammonium sulfid $(NH_4)_2S$, while those of the other metals are not. Thus we may divide Group II into two divisions.

Class A. As, Sb and Sn.

Class B. Hg″, Pb, Bi, Cu and Cd.

III. Precipitated by NH_4OH and not by the group reagents of the two groups preceding.

Fe, Al and Cr.

IV. Precipitated by $(NH_4)_2S$.

Ni, Co, Mn and Zn.

V. Precipitated by $(NH_4)_2CO_3$.

Ba, Ca and Sr.

VI. Includes all the metals not classed in the other five groups.

K, Na, NH_4 and Mg.

SEPARATIONS IN GROUP I. Pb, Ag and Hg.

For the purpose of practice the student should make a mixture of the soluble compounds of these three metals and then separate them. It is best to mix the nitrates.

1. To the solution containing the metals of G. I add HCl.

$PbCl_2$, AgCl and HgCl will be precipitated. Shake and allow the precipitate to settle. Add a few more drops of HCl to see if any more precipitate is formed.

2. Filter.

3. Wash precipitate on filter with a little cold water. When analyzing a solution containing metals of other groups than the first, this washing removes any solution that might cling to the

precipitate.

4. Wash precipitate with boiling water. $PbCl_2$ dissolves. The other chlorids remain on the filter. Test for lead with any of the reactions for that metal.

a. H_2SO_4 gives white $PbSO_4$.

b. K_2CrO_4 gives yellow $PbCrO_4$, etc.

5. Pour a little NH_4OH on the precipitate remaining. AgCl dissolves, forming $(NH_3)_3(AgCl)_2$ while the mercury turns black with formation of NH_2Hg_2Cl.

Confirm silver by adding nitric acid to the $(NH_3)_3(AgCl)_2$ until the solution is acid. White AgCl will be precipitated.

Confirm mercury by dissolving the black residue in aqua regia ($HCl+HNO_3$), evaporate nearly to dryness, take up with water and test as follows :

a. $SnCl_2$ gives a white precipitate, HgCl, which changes to black Hg on standing.

b. KI gives a red precipitate, HgI_2, soluble in excess of the reagent.

SEPARATIONS OF GROUP II.

A. As, Sb and Sn.

B. Hg'', Pb, Bi, Cu and Cd.

1. Into a solution containing the metals of group II, run H_2S at a moderate rate until no more precipitate is formed.

2. Filter and wash the precipitate with hot water.

3. Pierce a hole in the bottom of the filter paper and wash the precipitate into a small evaporating dish with enough $(NH_4)_2S_x$ to well cover it. Boil, and the sulfids of As, Sb and Sn will be dissolved.

4. Filter. The sulfids of class B will be in the filter paper, while those of class A have been dissolved and will be in the filtrate. Set aside the precipitate in the filter paper.

Class A. The sulfids of As, Sb and Sn have been dissolved, forming $(NH_4)_3AsS_3$, $(NH_4)_3SbS_3$ and $(NH_4)_3SnS_3$.

1. Make the solution acid with HCl.

As_2S_3, Sb_2S_3, SnS_2 will be precipitated. At the same time the excess of $(NH_4)_2S_x$ will be decomposed and large quantities of light yellow sulfur will be set free.

2. Filter and wash with hot water. Throw the wash water away.

3. Pierce the filter paper and wash the precipitate into a beaker with concentrated HCl.

4. Boil, and the sulfids of antimony and tin will dissolve, forming $SbCl_3$ and $SnCl_4$.

5. Dilute the acid solution and filter out the As_2S_3 which has not been dissolved.

6. Test the solution for antimony by placing in it a piece of platinum foil in contact with

a piece of zinc. The antimony will be precipitated as a black deposit on the foil.

7. For tin. Filter the solution from which the antimony has been removed. The $SnCl_4$ has been reduced to $SnCl_2$. Add $HgCl_2$ and if tin is present a white precipitate of HgCl is formed which will change to black Hg.

The action between the zinc and the platinum may have reduced the tin to the metallic form. In this case there will be no precipitate with $HgCl_2$. To make sure of the presence of tin remove the zinc and platinum. The tin will be in the form of a metallic precipitate on the bottom of the test tube. Pour off as much of the liquid as possible and dissolve this tin in HCl. Test as before with $HgCl_2$.

Class B. The metals of class B are present in the form of sulfids. Of these PbS, CuS, Bi_2S_3 and CdS are soluble in hot dilute nitric acid, while HgS is not.

1. Pour hot dilute HNO_3 through the filter paper several times. The HgS will remain while all the other sulfids are dissolved, forming $Pb(NO_3)_2$, $Bi(NO_3)_2$, $Cu(NO_3)_2$ and $Cd(NO_3)_2$.

For Pb, Bi Cu and Cd.

2. Evaporate the nitric acid solution nearly to dryness to remove the excess of acid and add a few drops of H_2SO_4. If lead is present it will be precipitated as white $PbSO_4$.

3. Filter out the $PbSO_4$ and add NH_4OH until the solution smells of ammonia. White $Bi(OH)_3$ will be precipitated. To confirm bismuth, dissolve this white precipitate in as little dilute HCl as possible and pour a few drops of this solution into a test tube of water. A white precipitate of BiOCl will be formed.

4. For Cu. If after adding the NH_4OH the solution has a deep blue color, copper is present. (See Copper, Exp. 17, 2.)

5. For Cd. If copper is not present run H_2S into the solution from which bismuth has been removed, and a yellow precipitate of CdS indicates Cd. If copper is present add KCN to the blue solution until the color disappears, then run in H_2S. A yellow precipitate will form as before. If this precipitate is dark colored it is probably due to the presence of Ag or Hg which have not been completely removed.

6. For Hg. Dissolve the precipitate on the filter paper with hot aqua regia. Evaporate the solution to dryness and take up with a little water. Test with

a. $SnCl_2$. Forms a white and then a black precipitate.

b. KI forms a red precipitate soluble in excess.

SEPARATIONS IN GROUP III.

Fe, Al and Cr.

The separation of the metals of group III is greatly complicated by the presence of phosphates, oxalates, silicates, borates and fluorids. If these acid radicals are in a solution containing the metals of group III and the following groups, Ba, Ca, Sr and Mg will precipitate with the third group. In the following scheme the consideration of phosphates, etc., has been purposely omitted.

1. If the solution containing group III metals is the filtrate from group II and contains H_2S, it must be boiled until it no longer has the H_2S odor.

2. If iron is present and the solution has been treated with H_2S the iron will be in the ferrous condition and will not precipitate completely with the reagent of the third group. To oxidize the iron to the ferric condition add a little HNO_3 and boil.

3. Add an equal volume of NH_4Cl, then NH_4OH in excess. The NH_4Cl serves two purposes. It causes the Al to precipitate completely and prevents the precipitation of Zn, Mn, Co, Ni and Mg. In analyzing an unknown which might contain the metals from all the groups these metals might be present and cause complications in group III.

4. The metals of group III are precipitated as $Fe(OH)_3$ (red brown), $Al(OH)_3$ (white), and $Cr(OH)_3$ (green).

5. Dissolve the mixed hydroxids in warm dilute HCl by pouring the acid on the precipitate in the filter paper. Add concentrated NaOH in excess and boil. The $Al(OH)_3$ will dissolve, forming $NaAlO_2$ (sodium aluminate), while the other hydroxids will remain in the precipitate. Filter and wash with hot water.

6. For Al.

Make the solution of $NaAlO_2$ slightly acid with HCl, then add NH_4OH. A white flocculent precipitate will indicate aluminum.

7. For Fe.

Divide the precipitate containing iron and chromium into two portions. Dissolve one in HCl and test for iron as follows:

a. With KSCN. A blood red color indicates Fe.

b. With $K_4Fe(CN)_6$. Blue color indicates Fe.

8. For Cr.

Mix the other portion with KNO_2 and Na_2CO_3 and fuse on platinum foil. A yellow residue of Na_2CrO_4 is formed. Dissolve this in hot water, make acid with acetic acid and add $Pb(C_2H_3O_2)_2$. A yellow precipitate of lead chromate will form. (See Cr, Exp. 30, 6.)

NOTE—Mn, Zn, Ni, Co and Mg will often appear in the third group and will confuse the tests. If this is the case, dissolve in HCl, add NH_4Cl and precipitate once more with NH_4OH.

SEPARATIONS IN GROUP IV.

Ni, Co, Mn and Zn.

All are precipitated as sulfids in an alkaline solution.

1. To the filtrate from group III or to a solution containing the metals of group IV add NH_4OH, then run in H_2S. $(NH_4)_2S$ is formed which precipitates the metals of the group as NiS (black), CoS (black), MnS (pink) and ZnS (white).

2. Filter and wash. Dissolve the MnS and ZnS in hot dilute HCl. Set aside the NiS and CoS which remain in the filter paper.

3. For Mn and Zn.

Boil the solution to free from H_2S.

Add NaOH in excess and boil. Mn is precipitated as $Mn(OH)_2$, while the zinc which is first precipitated as $Zn(OH)_2$ is dissolved in excess, forming Na_2ZnO_2. Filter.

4. For Mn.

Fuse some of the precipitate on platinum foil after mixing with Na_2CO_3 and KNO_3. Green sodium manganate will be formed. (See Mn, Exp. 39, 10.

5. For Zn.

Into the solution of Na_2ZnO_2 run H_2S. White

ZnS will precipitate.

For Ni and Co.

It is easy to identify either of these metals alone but their separation is a matter of some difficulty.

1. Test the black precipitate left after dissolving the Mn and Zn, with the borax bead.

Ni gives a brown bead.

Co gives a blue bead. If the two are mixed the blue of the Co will cover up the brown of the Ni.

2. To identify Ni in the presence of Co.

Dissolve the mixed sulfids in aqua regia, evaporate nearly to dryness and take up with water. Add KCN solution until the precipitate which forms at first goes into solution again. Add concentrated NaOH, boil and add bromin water. A black $Ni(OH)_3$ will be precipitated.

SEPARATIONS IN GROUP V.

Ba, Ca and Sr.

1. If the metals are in the filtrate from group IV, boil to free from H_2S. Add NH_4OH and, if a precipitate forms, add NH_4Cl until it dissolves. Add $(NH_4)_2CO_3$ and boil. $BaCO_3$, $SrCO_3$ and $CaCO_3$ are formed. The boiling makes the precipitation complete. Filter and wash.

2. For Ba.

Dissolve in acetic acid and add K_2CrO_4. The barium will be precipitated as $BaCrO_4$. Filter and wash. Set aside the filtrate for Sr and Ca.

To confirm Ba. Dissolve the $BaCrO_4$ in a little HCl and test the solution with H_2SO_4. White $BaSO_4$ will precipitate. Test another portion of the $BaCl_2$ solution with the flame.

3. The filtrate from 2 contains Sr and Ca in the form of acetates. To free from K_2CrO_4, precipitate again with $(NH_4)_2CO_3$, filter and wash the precipitate well.

4. Dissolve again in HCl and test with the flame. Sr gives a brilliant crimson and Ca a brick red color to the flame. There is great danger of confusing the two, so the test of an unknown should always be verified by comparison with a known sample. If both Ca and Sr are present the flame test will give confusing results.

NOTE—The Sr flame is very persistent, while the Ca flame lasts but a short time.

5. To the solution containing Sr and Ca add $(NH_4)_2SO_4$. Shake and allow to stand. $SrSO_4$ will precipitate a white, finely divided powder. The precipitate forms slowly, especially in dilute solutions. Filter. The filtrate contains $CaSO_4$, which is quite soluble in water.

6. For Ca.

Add to the filtrate from 5, ammonium oxalate, $(NH_4)_2C_2O_4$. White CaC_2O_4 will form.

NOTE—If NH_4Cl or other ammonium salts are present in large quantities, the complete precipitations of metals of group

V will be prevented. To free from ammonium salts, evaporate the filtrate from group IV to dryness in a porcelain dish, then heat the residue to dull redness. The salts will be decomposed. After ignition dissolve the residue in water with a little HCl. Add NH_4OH and $(NH_4)_2CO_3$, when the group will be precipitated.

GROUP VI.

Mg, NH_4, Na and K.

This group includes all the metals not precipitated by the reagents of the preceding groups. There is no group reagent so we must identify each metal by a special test.

1. For Mg.

Make the filtrate from group V alkaline with NH_4OH. If a precipitate appears add NH_4Cl until it is dissolved. Add Na_2HPO_4 and allow to stand for several hours in a warm place. Crystals of $MgNH_4PO_4$ will form on the sides of the containing vessel.

NOTE—Nearly all the metals of the preceding groups will form a precipitate with $NaHPO_4$, so if they have not been completely separated they will appear here. For that reason the student should not report magnesium unless the crystalline precipitate forms.

2. For NH_4.

To the original solution add NaOH and boil. The odor of ammonia indicates the compounds of ammonium.

3. For Na and K.

Test the original solution with the flame.

View the flame through a blue glass.

A brilliant yellow flame indicates Na.

A purple flame visible through blue glass indicates K.

NOTE—Na is often present in small quantities in the salts of other metals. Therefore, unless the test is brilliant, do not report sodium. If compounds of Cu, Ba, Sr and Ca are present they will interfere with the potassium test and must be removed by means of $(NH_4)_2CO_3$.

SUMMARY OF THE SEPARATIONS.

<table>
<tr><td colspan="6">1. Add HCl until no more precipitate is formed. Shake and filter.</td></tr>
<tr><td rowspan="5">PRECIPITATE.
GROUP I.
Lead $PbCl_2$
White
Silver AgCl
White
Mercury HgCl
Hg'
White
Separate as directed on pages 373-4.</td><td colspan="5">2. To the filtrate or, if Group I is absent, to the original solution plus HCl heat to boiling and add H_2S until the solution smells strongly of the gas. Warm and filter.</td></tr>
<tr><td rowspan="4">PRECIPITATE.
GROUP II.
Class A.
As_2S_3 Yellow
Sb_2S_3 Orange
SnS Brown
Class B.
PbS Black
Bi_2S_3 Black
CuS Black
CdS Yellow
HgS Black
Treat the whole precipitate with $(NH_4)_2S_x$ and proceed as directed on pages 374 to 377.</td><td colspan="4">3. Boil filtrate from 2 to expel H_2S, add HNO_3 and boil to oxidize the iron, add an equal volume of NH_4Cl, then NH_4OH to alkalinity. Filter.</td></tr>
<tr><td rowspan="3">PRECIPITATE.
GROUP III.
$Al(OH)_3$
White
$Fe(OH)_3$
Red brown
$Cr(OH)_3$
Green
Proceed as on pages 378-9.</td><td colspan="3">4. Into the ammoniacal filtrate from 3 run H_2S and filter.</td></tr>
<tr><td rowspan="2">PRECIPITATE.
GROUP IV.
NiS
Black
CuS
Black
MnS
Pink
ZnS
White
Proceed as on pages 360-1.</td><td colspan="2">5. Boil to free filtrate of 4 from H_2S, add NH_4OH and if a precipitate forms add NH_4Cl until it dissolves, then add $(NH_4)_2CO_3$; boil and filter.</td></tr>
<tr><td>PRECIPITATE.
GROUP V.
$BaCO_3$
White
$SrCO_3$
White
$CaCO_3$
White
Proceed as on pages 381-2.</td><td>6. GROUP VI.
The metals are Mg. NH_4, K, Na.
1. For Mg add to filtrate from 5 Na_2HPO_4. Crystalline $MgNH_4PO_4$ will be formed. See p. 383.
2. For NH_4 add NaOH to original solution, boil and note odor.
3. For K and Na try the flame test with the original solution. See p. 384.</td></tr>
</table>

THE ACID RADICALS.

The acids may be classified in three groups. This system of grouping depends upon the action of the acid radical with a reagent which is called the group reagent as in the case of the metals.

GROUP 1. Contains those acids which form a precipitate with $BaCl_2$ in a neutral solution. The most common representatives of this group are the following:

Sulfurous acid, H_2SO_3.
Sulfuric acid, H_2SO_4.
Thiosulfuric acid, $H_2S_2O_3$.
Chromic acid, H_2CrO_4.
Phosphoric acid, H_3PO_4.
Boric acid, H_3BO_3.
Hydrofluoric acid, HF.
Carbonic acid, H_2CO_3.
Oxalic acid, $H_2C_2O_4$.
Tartaric acid, $H_2C_4H_4O_6$.

GROUP 2. Contains those acids which form a precipitate with $AgNO_3$ in a solution slightly acidified with HNO_3. Such are

Hydrochloric acid, HCl.
Hydrobromic acid, HBr.
Hydriodic acid, HI.
Hydrocyanic acid, HCN.
Hydrosulfuric acid, hydrogen sulfid, H_2S.

Hydroferricyanic acid, $H_3Fe(CN)_6$.
Hydroferrocyanic acid, $H_4Fe(CN)_6$.
Sulfocyanic acid, HSCN.

GROUP 3. Contains those acids which do not fall in the above groups. Such are

Nitric acid, HNO_3.
Chloric acid, $HClO_3$.
Acetic acid, $HC_2H_3O_2$.

In this group may also be classified nitrous acid, HNO_2, which forms a precipitate with $AgNO_3$ only in concentrated solution. Arsenious and arsenic acid, H_3AsO_3 and H_3AsO_4, are indicated in the tests for the metals in group 2, class B.

COMMON REACTIONS FOR GROUP 1.

SULFUROUS ACID, H_2SO_3.

The free acid is very unstable, decomposing into H_2O and SO_2. Hence a solution of sulfurous acid will always have the odor of SO_2. For the reactions use a solution of a sulfite such as Na_2SO_3 or K_2SO_3.

1. $BaCl_2$ precipitates white $BaSO_3$. Easily soluble in HCl. If the sulfite has been partially oxidized to sulfate, as is usually the case, the precipitate will not completely dissolve.

2. $AgNO_3$ precipitates white Ag_2SO_3. On boiling this precipitate, black metallic silver will be formed.

3. $Pb(C_2H_3O_2)_2$ or as it may be written for brevity, $PbAc_2$ precipitates white $PbSO_3$. This is not decomposed by boiling. See thiosulfuric acid 2.

4. HCl and most mineral acids form free SO_2 which may be detected by the odor.

THIOSULFURIC ACID, $H_2S_2O_3$.

Use a solution of $Na_2S_2O_3$.

1. $BaCl_2$ precipitates white BaS_2O_3 from a concentrated solution. This is soluble in a large quantity of water.

2. $PbAc_2$ precipitates white PbS_2O_3. On boiling this forms black PbS.

3. $AgNO_3$ precipitates white $Ag_2S_2O_3$, soluble in excess of $Na_2S_2O_3$, forming $AgNaS_2O_3$. On heating, the $Ag_2S_2O_3$ changes to black Ag_2S.

4. HCl precipitates free sulfur, yellow white, and liberates SO_2.

SULFURIC ACID, H_2SO_4.

For the reactions use any solution of a sulfate.

1. $BaCl_2$ precipitates white $BaSO_4$, insoluble in all dilute acids.

2. $PbAc_2$ precipitates white $PbSO_4$. Easily soluble in ammonium acetate or tartrate.

CHROMIC ACID, H_2CrO_4.

The presence of chromic acid will be indicated in the third group of metals where the metal will be precipitated as a hydroxid.

For the reactions use a solution of K_2CrO_4.

1. $BaCl_2$ precipitates yellow $BaCrO_4$, insoluble in NaOH and acetic acid.

2. $PbAc_2$ precipitates yellow $PbCrO_4$, soluble in NaOH.

3. $AgNO_3$ precipitates red brown Ag_2CrO_4, solube in HNO_3 and NH_4OH.

4. $HgNO_3$ precipitates red Hg_2CrO_4, soluble in HNO_3.

5. HNO_3 turns the yellow solution of a chromate to the red dichromate such as $K_2Cr_2O_7$. In general the dichromate gives the same reactions as the chromate.

PHOSPHORIC ACID, H_3PO_4.

For the reactions use any soluble phosphate such as Na_3PO_4, etc.

1. $BaCl_2$ precipitates white $BaHPO_4$, soluble in dilute HCl.

2. $PbAc_2$ precipitates white $Pb_3(PO_4)_2$, soluble in HNO_3.

3. $AgNO_3$ precipitates yellow white Ag_3PO_4, soluble in NH_4OH and HNO_3.

4. Ammonium molybdate, NH_4MoO_4, precipitates yellow ammonium phospho-molybdate, $(NH_4)_3PO_4(MoO_3)_{12}$, soluble in NH_4OH. The precipitate forms slowly but is hastened by warming.

BORIC ACID, H_3BO_3.

For the common reactions use a solution of sodium pyroborate, $Na_2B_4O_7$.

Most of the salts formed by the common reagents are those of metaboric acid, HBO_2.

1. $BaCl_2$ precipitates white $Ba(BO_2)_2$ from a concentrated solution, soluble in NH_4Cl.

2. $AgNO_3$ precipitates white $AgBO_2$. If the solution is dilute the precipitate will be brown from the formation of Ag_2O.

3. $PbAc_2$ precipitates from concentrated solution $Pb(BO_2)_2$.

4. To a small quantity of borate solution in a porcelain dish or test tube add a little concentrated sulfuric acid and a little alcohol. Warm, and boric ether will be formed which on ignition burns with a green flame. This is the most characteristic test for a borate.

HYDROFLUORIC ACID, HF.

For the reactions use a solution of any soluble fluorid such as KF.

1. $PbAc_2$ precipitates white PbF_2, soluble in HNO_3.

2. A solid fluorid or a concentrated solution when treated with concentrated sulfuric acid will set free HF which will etch glass.

CARBONIC ACID, H_2CO_3.

For the reactions use a solution of Na_2CO_3. The free acid exists only in a very dilute solution.

1. $BaCl_2$ precipitates white $BaCO_3$. From

a generator lead CO_2 into the test tube containing the precipitate. In a short time it will dissolve forming $BaH_2(CO_3)_2$.

2. $PbAc_2$ precipitates white $PbCO_3$.

3. $AgNO_3$ precipitates light yellow Ag_2CO_3, soluble in NH_4OH.

4. HCl causes effervescence with a carbonate with formation of CO_2. This gas is heavier than air and may be decanted into a test tube containing a solution of $Ca(OH)_2$ which will form a white precipitate of $CaCO_3$.

OXALIC ACID, $H_2C_2O_4$.

Use a solution of $(NH_4)_2C_2O_4$.

1. $BaCl_2$ precipitates white BaC_2O_4 from a concentrated solution of an oxalate.

2. $PbAc_2$ precipitates white PbC_2O_4, soluble in HNO_3.

3. $AgNO_3$ precipitates white $Ag_2C_2O_4$, soluble in HNO_3 and NH_4OH.

4. $CaCl_2$ precipitates white CaC_2O_4, insoluble in acetic acid and NH_4OH, soluble in HCl.

TARTARIC ACID, $H_2C_4H_4O_6$.

Use a solution of sodium potassium tartrate, $NaKC_4H_4H_6$.

1. $BaCl_2$ precipitates white $BaC_4H_4O_6$ from concentrated solutions.

2. $PbAc_2$ precipitates white $PbC_4H_4O_6$, soluble in HNO_3 and NH_4OH.

3. To a quantity of a tartrate in a clean test tube add a few drops of $AgNO_3$ and a little NH_4OH. Warm on a water bath and a bright deposit of metallic silver will be formed on the walls of the tube. This is the most characteristic test for a tartrate.

GROUP 2.

HYDROCHLORIC ACID, HCl.

Dilute HCl or a solution of any chlorid may be used.

1. $AgNO_3$ precipitates white AgCl, soluble in NH_4OH and reprecipitated by HNO_3. Also easily soluble in KCN.

2. $HgNO_3$ precipitates white HgCl.

3. $PbAc_2$ precipitates white $PbCl_2$ from a moderately concentrated solution. This is soluble in hot or in a large quantity of cold water, hence if the solution is dilute the precipitate will not appear.

HYDROBROMIC ACID, HBr.

Use a soluble bromid such as KBr.

1. $AgNO_3$ precipitates light yellow AgBr, soluble in NH_4OH although not so easily as the AgCl. Easily soluble in KCN. Reprecipitated from solution by HNO_3.

2. $PbAc_2$ precipitates white $PbBr_2$. This is somewhat soluble in water but not so easily as $PbCl_2$.

3. $HgNO_3$ precipitates yellow white HgBr.

4. Chlorin sets the bromin free from a solution of a bromid. Hence if chlorin water is added to a bromid solution the bromin will be set free and the solution will become reddish brown. Add a few drops of CS_2 and shake. The bromin will dissolve in the reagent and will color it brown.

HYDRIODIC ACID, HI.

Use a solution of KI.

1. $AgNO_3$ precipitates light yellow AgI. Slightly soluble in NH_4OH but soluble in KCN. Insoluble in HNO_3.

2. $PbAc_2$ precipitates yellow PbI_2, soluble in hot water from which it will crystallize on cooling in golden yellow crystals.

3. $HgNO_3$ precipitates yellow green HgI.

4. $HgCl_2$ precipitates scarlet HgI_2, soluble in an excess of KI.

5. Chlorin water liberates iodin from its compounds. Repeat Exp. 4 under HBr with KI and the CS_2 will be colored a beautiful violet.

HYDROCYANIC ACID, HCN.

For the tests use a solution of KCN.

1. $AgNO_3$ precipitates white AgCN, soluble in an excess of KCN and in NH_4OH. From these solutions it is precipitated by HNO_3.

2. $PbAc_2$ precipitates white $Pb(CN)_2$, insoluble in KCN.

3. $CuSO_4$ precipitates green $Cu(CN)_2$, soluble in KCN. From this solution H_2S will not precipitate the Cu. See separation of copper and cadmium in the second group of metals.

4. To a solution of a cyanid add a few drops of $(NH_4)_2S_x$ and boil. This forms KSCN. Make acid with HCl and add a little $FeCl_3$. A blood red coloration due to $Fe(CNS)_3$ will be formed.

HYDROSULFURIC ACID, H_2S.

Use a solution of Na_2S or K_2S.

1. $AgNO_3$ precipitates black Ag_2S, soluble in HNO_3.

2. $PbAc_2$ precipitates black PbS, soluble in HNO_3.

3. $SbCl_3$ precipitates orange red Sb_2S_3; soluble in $(NH_4)_2S_x$.

5. A solution of a sulfid treated with HCl or H_2SO_4 will be decomposed, liberating H_2S which is easily recognized by the odor.

HYDROFERRICYANIC ACID, $H_3Fe(CN)_6$.

Use a solution of $K_3Fe(CN)_6$.

1. $AgNO_3$ precipitates red brown $Ag_3Fe(CN)_6$, soluble in NH_4OH.

2. $FeSO_4$ precipitates blue $Fe_3[Fe(CN)_6]_2$. This is called Turnbull's blue. Insoluble in HCl.

3. $FeCl_3$ gives a dark blue solution but no precipitate.

HYDROFERROCYANIC ACID, $H_4Fe(CN)_6$.

Use a solution of $K_4Fe(CN)_6$.

1. $AgNO_3$ precipitates white $Ag_4Fe(CN)_6$, insoluble in dilute NH_4OH.

2. $PbAc_2$ precipitates white $Pb_2Fe(CN)_6$.

3. $CuSO_4$ precipitates red brown $Cu_2Fe(CN)_6$. This is a very delicate reaction and can be shown in a very dilute solution.

4. $FeCl_3$ precipitates $Fe_4[Fe(CN)_6]_3$, Prussian blue.

SULFOCYANIC ACID, HSCN.

Use a solution of KSCN.

1. $AgNO_3$ precipitates white AgSCN, soluble in NH_4OH.

2. $CuSO_4$ precipitates from concentrated solutions black $Cu(SCN)_2$. If H_2SO_3 is added in excess to a solution of a sulfocyanid and boiled, $CuSO_4$ will precipitate white $Cu_2(SCN)_2$.

3. $FeCl_3$ forms blood red $Fe(SCN)_3$. This is very characteristic.

GROUP 3.

NITRIC ACID, HNO_3.

Use nitric acid or any solution of a nitrate. All nitrates, chlorates and acetates are soluble in water.

1. The "Brown Ring" test. To a solution of a nitrate add an equal volume of $FeSO_4$ solution.

Incline the test tube and allow some concentrated H_2SO_4 to run down the side. If the experiment is carefully carried out the acid will collect at the bottom of the tube and at its upper surface a brown ring will form which is due to NO_2 dissolved in $FeSO_4$. This reaction is very characteristic.

2. The NO_2 test. To a nitrate add concentrated H_2SO_4 and a small piece of copper. HNO_3 is set free, this combines with the copper and brown NO_2 is formed.

CHLORIC ACID, $HClO_3$.

Use a solution of $KClO_3$.

1. If a solid chlorate is treated with concentrated H_2SO_4 the two will combine with explosive violence. See the tests for a chlorate under blowpipe analysis.

2. A solution of a chlorate with HCl gives chlorin and chlorin peroxid as follows:

$$2HCl+KClO_3=KCl+H_2O+ClO_2+Cl.$$

Test the chlorin by the odor and by its bleaching effect on moist litmus paper.

The chlorates form no precipitates.

ACETIC ACID, $HC_2H_3O_2$.

Use a solution of $NaC_2H_3O_2$.

1. To a solution of an acetate add concentrated H_2SO_4. Note the vinegar like odor. To the solution containing H_2SO_4 add a little alcohol,

C_2H_5OH. Boil and note the apple-like odor. This is due to the formation of ethyl acetate, CH_3COO-C_2H_5.

2. $FeCl_3$ gives a deep red color to a neutral solution of an acetate. On boiling red-brown basic ferric acetate is formed, $Fe(OH)_2C_2H_3O_2$.

NITROUS ACID, HNO_2.

The acid does not exist in the free state. It is best known in the form of its potassium salt, KNO_2. For the reactions use this salt.

1. $Co(NO_3)_2$ to which acetic acid has been added precipitates yellow $Co(NO_2)_3(KNO_2)_3$. $NaNO_2$ does not give this reaction.

2. To a solution of a nitrite add a little KI and starch paste. On adding a few drops of H_2SO_4 iodin is liberated and the starch is turned blue. CS_2 may be used instead of the starch paste.

3. On adding an acid such as H_2SO_4 to a solution of a nitrite copious brown fumes of NO_2 will be liberated.

The systematic separation of the acids is a rather difficult matter and beyond the scope of a small text. For separations the student is referred to the larger works on qualitative analysis.

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